

A COLLEGE COURSE
OF
INORGANIC CHEMISTRY

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PREFACE

THE present work is in some ways an abridgment of the larger *Text-Book of Inorganic Chemistry for University Students*, which first appeared in 1921 and is now in a fifth edition. The *Text-Book* has been used in school and college courses of Intermediate and Higher Certificate standard, although it goes beyond these requirements. The present book is intended to meet the needs of students of this standard in Inorganic and Physical Chemistry. Although the general plan and method of treatment of the *Text-Book* have served as a foundation, the text has been very largely rewritten and rearranged.

A certain maturity of outlook and a corresponding ability to use scientific language are expected of students at this stage. They should be able to express themselves in a clear, accurate and concise way, and any course of study which fails to inculcate this habit of thought must be regarded as unsatisfactory. It is hoped that the style of the text will serve as a guide to this end. Although the examinations have been kept in mind, no part of the text has been curtailed to what might be reproduced by a weak candidate in a given time, since it is obviously better to give a clear and adequate presentation of each topic than an incomplete passage which might be memorised. Any student who really understands a subject will produce a better and more concise answer than one who has merely memorised a consciously abridged statement.

Three prevalent faults in the answers of Higher Certificate candidates are : (1) failure to give equations, (2) inadequate experimental detail, and (3) the omission of diagrams. An attempt has been made to provide material for satisfactory answers in these three respects. The author's work as an examiner has disclosed two main faults in Higher Certificate and Intermediate candidates, namely, (1) far too many candidates achieve a bare pass, showing that their preparation has been inadequate and the standard aimed at too low, and (2) a large proportion of the candidates are unfamiliar with the more elementary parts of the subject, of School Certificate standard. An attempt has been made to provide a course of adequate standard and also to deal with the elementary parts of the subject in sufficient detail for revision purposes. The last provision is also important for candidates who enter the university to prepare for the Intermediate and First Medical examinations with no

previous training in Chemistry. Experience shows that such students, if suitably taught, usually make very satisfactory progress, and as they very often have no knowledge of Physics this has been kept in mind in the sections on Physical Chemistry. The book is intended to be suitable for rather older students who are beginners as well as for younger pupils who have reached School Certificate standard.

The general arrangement of the book is as follows. After an introduction to the general principles of the subject, and a revision of more elementary topics, the elements oxygen, hydrogen and the halogens, and their compounds, are dealt with. This makes clear the relation between elements in a group and, after some chapters on Physical Chemistry, a study of the Periodic Law can be taken up. This involves the mention of many more elements than are dealt with at this stage, but unless the student realises that the Periodic Table is a summary of the relations of *all* the elements he will miss its real significance. The section on atomic structure and the electronic theory of valency is not necessary for some examinations, but in others questions on these subjects are regularly set.

After the chapter on the Periodic Law, the elements are described in the order of the groups in the Periodic Table, non-metals and metals being taken together, and in each section there is a definite order, the history, occurrence, preparation and properties of the element, and the preparation and properties of its compounds, also in the order of the groups (except that the oxides usually follow the halogen compounds), being dealt with. Many teachers will vary this order, and every arrangement has some disadvantages as well as advantages. Such a systematic arrangement, however, is one which lends itself most easily to variation. The author believes that for elementary students a definite plan and order is superior to an arbitrary arrangement of topics. At a later stage, a different arrangement may be better, but for less advanced students a systematic order has great advantages.

The subjects dealt with are intended to come within the scope of students whose knowledge is to reach Intermediate standard, and the mode of treatment is similarly adapted to this purpose. One often hears the statement that a knowledge of what are called "general principles" is more important than a knowledge of details. In Chemistry, however, where all the topics are interlinked, general principles must necessarily be based on an adequate knowledge of details, unless they are merely memorised without being understood. Out of the vast range of Chemistry, a small field has been selected for study at this stage, and examiners expect that this small field shall be adequately covered. Attempts to classify small fragments of the field as more or less "important" are

misplaced. Except in Organic Chemistry, inferences drawn from generalisations are often incorrect, and examiners are all too familiar with the results of such a procedure on the part of weak candidates.

Many students find it useful to make tabular statements, the preparation of which can afford a valuable training. The provision of such ready-made digests in a text-book, however, takes away most of their advantages and debases their use to mere memorising.

Suitable accounts are given of industrial processes and of the uses of important substances, and in this way the interest of students in everyday substances can be stimulated. More examination questions requiring such knowledge might well be set. It is not always realised that modern chemical and metallurgical industry has reached such a stage of perfection that some materials are produced on the large scale with a purity which is attained only in the best chemical laboratories.

Relatively few numerical examples are given, since this part of the subject has been fully dealt with in the book *Intermediate Chemical Calculations* by the author and Mrs. K. Stratton. The ability to work such calculations is a very desirable result of a course of study. A selection of recent examination questions is given, and these have been arranged in the order of the chapters. It must be remembered, however, that questions of common occurrence involve material from several chapters, and if the complete answer is not in the chapter to which a question is attached, part of the question may be attempted and the other parts noted and left for a later stage.

Careful attention has been given to the Physical Chemistry required at this stage. In this branch, Higher Certificate candidates are often very weak, no attempt being made to grasp the *quantitative* aspect of the subject and to acquire facility in working examples. Here again, although worked examples have been given in all important cases, detail has been omitted as it will be found in *Intermediate Chemical Calculations*. The subject of ionic equilibria has been treated from the modern point of view.

The historical approach has often been used, since the author has found it to give very good results in teaching over many years. It introduces an element of interest and reality which otherwise may be difficult to achieve, and it teaches the valuable lesson that scientific truth is something which has not only grown, but is also still growing. Most examining bodies expect an elementary knowledge of the history of the subject, and many students derive benefit from reading some of the great classics of chemical science. References to these in accessible reprints are, therefore, often given. As many teachers find it stimulating to develop some aspects of the general course in more detail, references to books and

papers which may be consulted by the teacher and the keener students are given in several cases.

I have pleasure in expressing my thanks to Sir Richard Gregory, Bt., F.R.S., who has given valuable advice and help in deciding the general scope and character of the book, and to Mrs. K. Stratton, M.Sc., who has given me assistance in arranging the questions, providing the numerical answers, and helping with the index.

J. R. PARTINGTON

WEMBLEY PARK, MIDDLESEX

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CHAPTER I

PURE SUBSTANCES, MIXTURES AND SOLUTIONS

Composition of materials.—One of the most obvious facts is that very many things differ completely in their essential characters or properties.

A house is constructed of various kinds of **stone**, bricks, different woods, iron, concrete, slates, tiles, plaster, mortar, **and** glass. The furniture and fittings inside consist of other kinds of wood, of different metals such as lead, copper, brass, bronze and aluminium; **and** in the various rooms will be found miscellaneous articles made of such **materials** as ebonite, celluloid, porcelain, wool, cotton, silk, tinsplate, silver **and** gold, together with various kinds of food, oil, coal, drinking water, candles **and** gas. The contents of the druggist's shop, of the oil and colour store, and of the garage, dyes, paints, varnishes, enamels, explosives, and the bitumen on roads are all different materials. The world of Nature, with its rocks, minerals, plants and animal life, presents another picture of the apparently endless variety of materials which we encounter at every turn. These differences exist, as we realise, quite apart from any particular shape or size which has been given to the objects.

We summarise these differences in essential properties by saying that **things may differ in composition**. Sugar and salt are two materials of different composition; a lump of sugar and powdered sugar are two different forms of the same material.

In a chemical laboratory the student will find a large number of materials (commonly called "chemicals") which are not met with in everyday life. There will be bottles containing white and coloured crystals and powders and various kinds of liquids. Among the things which every student of chemistry must learn are the appearances, properties and uses of common laboratory substances. *Every material used in practical chemistry should be carefully examined*: its colour, crystalline form and density (*i.e.* whether it is heavy or light, as judged by the weight of the bottle containing it) should all be noticed.

Substances which do not crystallise are called **amorphous**: powdered charcoal, magnesium oxide, and some kinds of manganese dioxide are **amorphous** powders, and glass is an **amorphous** solid. Some powders

are really composed of very small crystals, which may often be recognised under a lens or a microscope.

Mixtures.—Crystals of copper sulphate, common salt, etc., when purified (say by crystallisation from water), are examples of what is called a **pure substance**, as contrasted with a **mixture** (sometimes called a “mechanical” mixture; the scientific name is a **heterogeneous body**) such as a mixture of salt and sand, or of iron filings and sulphur. Every mixture is composed of at least two separate things existing in particles lying side by side. In some cases these can be seen only with the microscope, as when the powder is very fine. Each particle of one substance is sharply defined from the particles of the other substances.

A powder of a pure substance, *e.g.* sulphur, on the other hand, is composed of particles which are all alike, hence it is called, scientifically, a **homogeneous body**.

The first step in reducing the great variety of materials to a system is clearly that of separating mixtures into their homogeneous constituents.

The separation of mixtures.—The methods used in this separation include hand-picking when the mixture is coarse-grained; magnetism when one of the materials is attracted by a magnet and the others not, such as iron filings from a mixture with sulphur; and sedimentation when one constituent (*e.g.* iron filings) is heavier than the other (*e.g.* sulphur): the mixed powder is stirred up with water, and the heavier part is allowed to sink while the lighter is washed away. Finally, we can sometimes effect separation by *dissolving* out one constituent and leaving the others, as when salt is dissolved from its mixture with sand by stirring with water in a beaker. Sulphur is separated from a mixture of iron filings and sulphur by shaking in a corked test-tube with carbon disulphide,* which dissolves sulphur. Filtration will separate the *solution* from the insoluble residue.† The dissolved substance is obtained from the filtrate by evaporation.

In some cases the dissolved substance is obtained in crystals by evaporating until crystals form when a drop of the liquid is taken up on a glass rod and placed on a dry watch-glass. The bulk of the liquid is then allowed to cool. Large crystals are formed when crystallisation takes place slowly. Very large crystals of alum, for example, may be obtained by allowing a solution saturated at the ordinary temperature to evaporate slowly in the air, and suspending a small perfect crystal in the solution by a thread. If a hot solution is cooled rapidly and stirred, small crystals are deposited. These are usually purer than the large crystals,

* Carbon disulphide is a volatile *very inflammable* liquid with a disagreeable smell, and care must be taken in using it.

† Details of filtration, etc., are given in the author's *School Course of Chemistry*, Chapter I.

since they are less likely to include liquid. The crystals are separated by filtration. When as much liquid has drained off as possible, the filter paper is removed from the funnel, opened out, and laid on a piece of card or a porous plate, and the crystals allowed to dry in the air at the ordinary

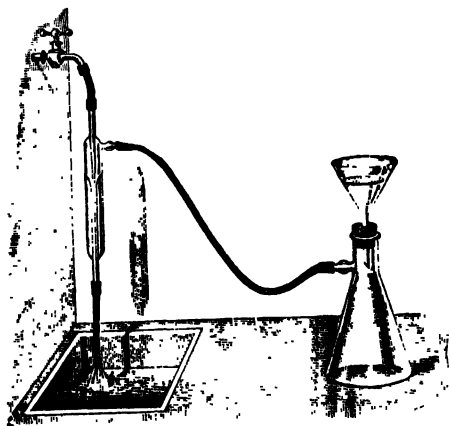


FIG. 1.—Filter pump and filter flask.

temperature. The last portions of solution (called *mother liquor*) adhering to the crystals are best removed by transferring the crystals from the dish by means of a spatula to a filter paper laid on a perforated porcelain plate in a filter funnel attached to a filter flask. This is connected with a filter pump, which draws air from the flask (Fig. 1). The crystals are then pressed with the spatula and when no more liquid runs from them they are dried as described above.

The drying may sometimes be completed in a desiccator (Fig. 11) or by heating in a steam oven, which is a copper oven with a steam jacket. Many crystals, however, lose water and fall to powder when so treated (p. 8).

Solutions.—Water will *dissolve* many solids such as sugar or salt to form solutions (Fig. 2). These contain the dissolved substance or *solute* in an extremely finely divided form, uniformly distributed through the liquid. The crystals in contact with the water first dissolve to produce a *saturated solution*, containing as much sugar or salt as the water will dissolve in the circumstances; if this is mixed with the pure water above the crystals by stirring, solution is more rapid.

Water is a useful solvent, *i.e.* a substance (generally liquid) which dissolves other substances. Many things are insoluble in water:

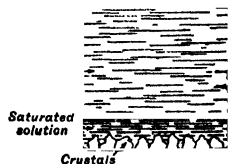


FIG. 2.—Solid dissolving in a liquid.

e.g. oil, wax, sulphur. Oil and grease are easily soluble in benzene or petrol, which are used in dry-cleaning soiled clothes.

Distillation.—Liquids containing dissolved solids are purified by distillation. A simple apparatus for this is a glass retort with the neck passing into a glass flask or receiver, which is cooled by water (Fig. 3).

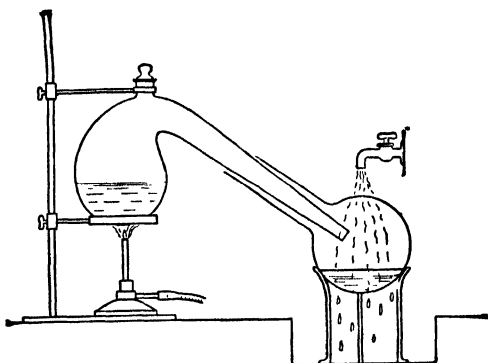


FIG. 3.—Retort and receiver for distillation.

The dissolved solid (*e.g.* salt in sea water) remains in the retort when the liquid is boiled, but the water passes over as steam, which condenses to pure water in the cooled receiver.

When larger quantities of liquid are distilled it is more convenient to use a flask attached to a Liebig's condenser (Fig. 4), consisting of a glass

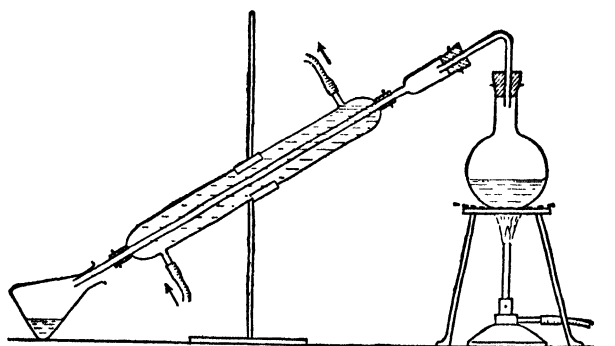


FIG. 4.—Apparatus for distillation, with Liebig's condenser.

tube enclosed in a jacket through which a constant stream of cold water is passed in the direction shown. A thermometer may be fitted through the cork of the flask, with the bulb suspended in the *vapour* coming from

the boiling liquid, or else a special distillation flask (Fig. 83) is used. With this apparatus not only solutions of solids in liquids but also solutions of liquids in liquids may be separated, at least in part. Thus if a mixture of equal volumes of alcohol (boiling point 78°) and water (b. pt. 100°) is distilled, it begins to boil at 84° and the liquid collecting in the receiver is richer in alcohol than the original mixture; it will burn when lighted in a dish. If the distillation is stopped when one-fourth of the mixture has distilled over and the distillate poured into a clean flask, it begins to boil at 81.5° , *i.e.* at a lower temperature than the original mixture, and the first portion of the distillate is correspondingly richer in alcohol. This partial separation of liquids is called **fractional distillation**.*

Solutions of gases in liquids.—It is easy to prove that liquids can dissolve gases. A large flask fitted with a cork and delivery tube is completely filled with rain water or tap water, the delivery tube being also filled with water. (The delivery tube should not project below the cork in the flask.)

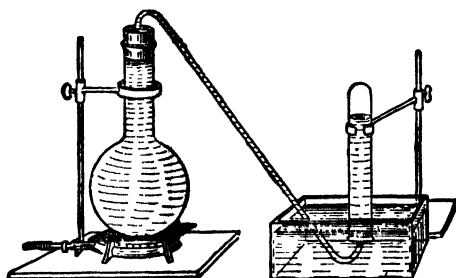


FIG. 5.—Separating air dissolved in water.

The flask is heated: bubbles of air pass out of the delivery tube under water and are collected in a test-tube (Fig. 5).

Solutions of liquids in liquids.—Some liquids such as water and oil are practically **immiscible**, that is they will not mix together; others such as water and alcohol will mix together in all proportions, that is they are **completely miscible**. In some cases such as ether and water, each liquid dissolves a limited amount of the other, or the liquids are **partially miscible**; two liquid layers are formed and may be separated by means of a **separating funnel** (Fig. 6). The heavier liquid is run off through the tap and the lighter liquid remains in the funnel.



FIG. 6.—Separating funnel.

The presence of ether in the lower layer may be shown by heating it in a test-tube, when the ether vapour given off may be kindled. The presence of water in the upper (ether) layer may be shown (after separating it from the lower layer and pouring it into a dry test-tube) by dropping a bit of sodium into it, when an inflammable gas hydrogen is evolved. Pure ether has no action on sodium.

If a little iodine is added, which dissolves in each solvent, it is found on shaking that the iodine is shared between the two liquids but most of it is taken by the ether, as is seen from the darker brown colour of the solution.

Solutions of solids in liquids.—The most important solutions are those of solids in liquids. Common salt added to water dissolves up to a certain point; after this, salt no longer dissolves, but settles out unchanged.

When a solution can exist unchanged in contact with the solid which is partly in solution, it is said to be **saturated**.

A solution which will dissolve more solid when brought in contact with it is called **unsaturated**.

Since a saturated solution will remain unchanged in contact with solid it is said to be in **equilibrium** with the solid.

The statements that “a saturated solution is one which has dissolved as much solid as possible”, or that it “contains as much solid as the liquid can dissolve”, are very common errors easily proved to be incorrect.

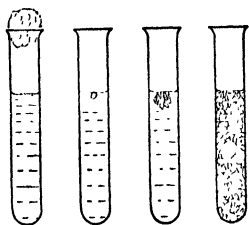


FIG. 7.—Crystallisation of a supersaturated solution.

A large test-tube is half filled with crystals of sodium thiosulphate (“hypo”) and the neck is plugged with cotton wool. The tube is heated in a beaker of boiling water. The salt melts in its own water of crystallisation to a very concentrated solution. On cooling this remains liquid; it is then a **supersaturated** solution. On removing the plug and dropping into the liquid a crystal of hypo, the liquid at once begins to solidify and the mass becomes warm, since heat is evolved in the process. Supersaturated solutions invariably crystallise in contact with the solid form of the solute. The crystallisation is seen to spread from the crystal of solid dropped in (Fig. 7).

Solubility.—Solutions are commonly called “strong” or “weak” according as they contain more or less dissolved substance. A more scientific way of stating this is to say that they are “concentrated” or “dilute”, and to give the number of grams of substance dissolved in 100 grams of water (or other solvent). This figure, in the case of a **saturated** solution, is called the **solubility**.

The **solubility** is the number of grams of solute dissolved by 100 grams of solvent at a given temperature in presence of excess of solute.

For example, the solubility of common salt in water is 35.9 at 15°, since 100 grams of water at this temperature are saturated by 35.9 grams of the salt.

Many salts crystallise from water as compounds containing water of crystallisation, called **hydrates**. Each hydrate (if more than one exists,

as frequently happens) has its own definite solubility, but in all cases the result is expressed in terms of salt free from water (anhydrous salt) contained in the solution per 100 grams of water.

Solubility depends (1) on the chemical characters of the solute and solvent, *e.g.* common salt is less soluble than "hypo" in water and both salts are nearly insoluble in alcohol; (2) on the temperature, generally but not always increasing with rise of temperature; (3) on the pressure, although this has very little effect except with gases (p. 68).

The way in which solubility depends on temperature is most conveniently represented graphically by means of solubility curves in which solubilities are plotted against temperatures.

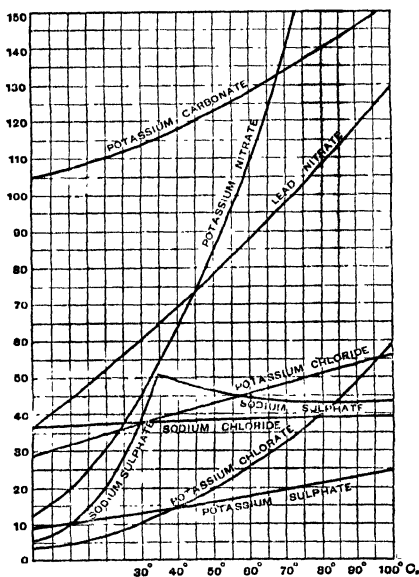


FIG. 8.—Solubility curves.

Fig. 8 shows the solubility curves of some salts in water at different temperatures. It is seen that these vary very much. The solubilities of some salts (*e.g.* potassium nitrate) increase rapidly as the temperature rises. A few salts, such as sodium chloride (common salt), are not much more soluble at higher temperatures than at room temperature, and sodium sulphate becomes less soluble at higher temperatures.

The sharp break in the sodium sulphate curve is caused by the change of the solid hydrate (Glauber's salt) into anhydrous sodium sulphate at 32.4° . Gypsum (hydrated calcium sulphate) increases in solubility up to 40° and then decreases at higher temperatures.

Measurement of solubilities.—An *approximate* determination of solubility can be made by adding a weighed amount of the finely powdered salt to a measured quantity of water not quite sufficient to dissolve it at a given temperature, then raising the temperature slowly until the solid is *almost* completely dissolved in the well-stirred solution. The temperature is then read off and one point on the solubility curve is found. Further weighed amounts of powdered salt are added one after the other, and the temperature raised until each portion is almost completely dissolved.*

A more accurate method is to stir an excess of the powdered salt with water at a given temperature so that the solution becomes saturated. Some of the clear solution is removed by a dry pipette fitted with a short piece of tubing packed with glass wool to serve as a filter, and a clip and rubber tubing at the top. The filter is removed and the liquid in the pipette is run into a weighed stoppered weighing bottle, which is weighed when cold. The contents of the bottle are transferred to a weighed dish and evaporated on a steam bath. The weight of the dry residue is found.

In accurate experiments, an excess of powdered solid is stirred for some time by a glass stirrer (driven by a motor) with water in a bottle which is supported in a *thermostat* (a water bath maintained at a constant temperature by a thermoregulator). A portion of solution is then taken out as described above.†

When the salt is only very slightly soluble such methods are not accurate enough, and the amount in solution is then found in some other way, for example by measuring the electrical conductivity of the solution (see Chapter XVII). In some cases the salt cannot be dried without decomposition and the amount in solution can then be found by chemical analysis, for example by volumetric titration or gravimetric analysis by precipitation.

Hydrates.—Large clear crystals of washing-soda when exposed to the air become white and opaque and fall to powder. There is also loss in weight. The change is due to loss of water from the crystals, and is called *efflorescence*.

Many salts form crystals containing salt and water in a definite ratio and are called *hydrates*.‡ The chemically combined water of hydration is usually known as *water of crystallisation*.

The presence of water in a crystal hydrate may be shown by the apparatus of Fig. 9. A quantitative experiment may be made by heating

a weighed amount of the crystals in a weighed dish in an air-oven (a copper oven heated by a bunsen or electrically) until the weight is constant. Sometimes (*e.g.* with gypsum crystals) a rather high temperature is necessary and the substance is then heated in a weighed crucible. Sometimes the salt decomposes on heating and the water is then usually found by difference from a chemical analysis.

A salt hydrate may usually be rendered anhydrous by heating, when the water of crystallisation is driven off. The blue crystals of hydrated copper sulphate (*blue vitriol*) on heating gently fall to a white powder of a lower hydrate and on heating more strongly this loses water to form the anhydrous salt. This at once takes up water and becomes blue when moistened and also slowly turns blue on exposure to moist air from absorption of moisture. The white powder is used in testing "absolute" alcohol for water; if water is present the powder becomes blue when shaken with the alcohol.

Some substances (*e.g.* sal ammoniac, sulphur and iodine) when heated in a test-tube pass into vapour which condenses again on the cool part of the tube. This is called **sublimation**. Strictly, this name should be used for solids (*e.g.* sal ammoniac) which pass into vapour without first melting, but it is commonly used when the solid (*e.g.* sulphur or iodine) first melts.

Efflorescence.—If a crystal of a hydrated salt such as washing-soda is passed into the vacuous space of a barometer tube the mercury sinks,

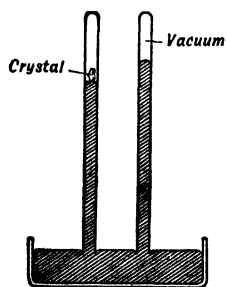


FIG. 10.—Vapour pressure of a crystal hydrate.

(Fig. 10). If this is greater than the pressure of the water vapour in the atmosphere the crystal will lose water on exposure and effloresce. The rapidity of efflorescence is increased by heating the crystal, since this increases the pressure of water vapour, and also by placing the crystal in a desiccator, since the water vapour is then able to escape more rapidly, although the pressure remains the same. The increase in vapour pressure when the temperature is raised can be shown by putting a hot-water jacket round the upper part of the barometer tube.

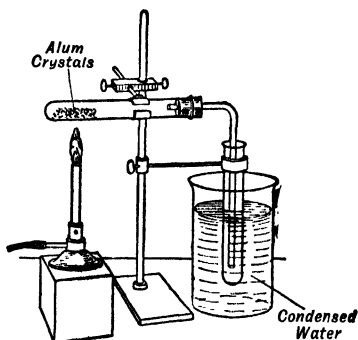


FIG. 9.—Effect of heat on alum crystals.

The desiccator.—Solids are dried by keeping them in air over a drying agent (calcium chloride, quicklime, concentrated sulphuric acid, or phosphorus pentoxide) which readily absorbs water vapour, contained in a closed glass vessel called a **desiccator** (so called from the Latin *siccus*, dry; the student should note the spelling of desiccator). A common form is shown in Fig. 11. The drying agent is in the lower half and the lid is an accurate fit on a ground flange which is greased. The substance to be dried or kept dry is contained in a crucible or other vessel.

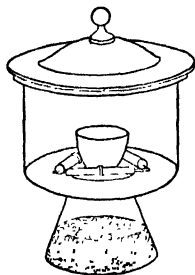


FIG. 11.—Desiccator.

In some cases the desiccator is fitted with a tap through which air may be removed from it by means of a filter pump (Fig. 1). In such a "vacuum" desiccator drying is more rapid than in air.

Solids which absorb moisture from the air and so become damp and finally liquid are called **deliquescent** (*e.g.* calcium chloride). Solids which absorb moisture from the air without becoming damp or liquid (*e.g.* quicklime), and also liquids which take up atmospheric moisture (*e.g.* concentrated sulphuric acid), are called **hygroscopic**. Some hygroscopic substances (*e.g.* recently ignited charcoal) take up moisture by a physical not a chemical process.

Fractional crystallisation.—Just as fractional distillation (p. 5) is used in the separation of liquids of different boiling points, so **fractional crystallisation** may be used in the purification and separation of solids having different *solubilities*. Particular use is made of the fact that the solubilities of some salts increase more rapidly with rise of temperature than the solubilities of other salts.

Fractional crystallisation is an important method and the complete theory is rather complicated. A general idea of the principle may be gained from the solubility curves in Fig. 8.

Consider a mixture of potassium nitrate and sodium chloride. 100 gm. of water at 65° dissolve 120 gm. of potassium nitrate but only 37 gm. of sodium chloride. If a mixture of equal parts of the two salts is heated with a suitable amount of water insufficient to dissolve all the sodium chloride, the whole of the potassium nitrate will go into solution, together with some sodium chloride.

Now let the solution be poured off from the undissolved sodium chloride, and allowed to cool to 15°. At this temperature 100 gm. of pure water is saturated by 25 gm. of potassium nitrate, so that a considerable amount of this salt will separate from the solution. A small amount of sodium chloride will also separate, since its solubility at 15° is about 36. This small amount of sodium chloride may be removed from the potassium

nitrate either by repeating the process of crystallisation, when all the sodium chloride will remain in solution, or by washing the crystals with *ice-cold* water, in which potassium nitrate, as is seen from the curves, is much less soluble than sodium chloride, so that the latter is removed.

The solubility of a salt in a solution of another salt is not the same as in pure water, and the difference is much greater when the two salts have a common acid or base. It is, therefore, not possible to calculate the amount of each salt dissolved from a mixture by making use of the solubilities of the pure salts.

CHAPTER II

CHEMICAL AND PHYSICAL CHANGES

Chemical changes.—Bodies often undergo very marked and permanent changes under certain conditions. Thus milk may become sour ; bright copper becomes dull and ultimately covered with a green crust when exposed to moist air, and under the same conditions iron rusts away completely to a brown powder. A candle burns away, and apparently disappears. A piece of copper wire becomes covered with black scales when heated, whilst a piece of magnesium ribbon on heating in a bunsen flame takes fire and burns brilliantly, leaving a white ash.

In other cases the changes appear to be less marked, and the properties of the materials are only slightly and temporarily modified. Thus, water on cooling freezes to ice, but the ice melts and is reconverted into water on warming. A bar of iron which has been heated to redness is only slightly altered and, apart from a little scale on the surface, is recovered without change on cooling. A piece of platinum wire when heated in a bunsen flame becomes red hot, but is unchanged on cooling.

Material changes either (i) alter only a few properties of the material and are temporary, when they are called **physical changes** ; or (ii) they lead to a complete alteration of properties and the formation of a different material, when they are called **chemical changes**, or **chemical reactions**.

Experiments on chemical changes.—The following experiments illustrate some striking chemical changes.

(1) A small piece of white phosphorus placed on a sand-tray is sprinkled with a few crystals of iodine. The phosphorus takes fire.

(2) Dilute solutions of potassium ferrocyanide, tannin and potassium thiocyanate, all practically colourless, are poured into three glasses and a very dilute solution of ferric chloride acidified with a little hydrochloric acid, also practically colourless, is added. Blue, black and red solutions are formed.

(3) A small pill of mercuric thiocyanate heated by the flame of a taper swells up into a worm-like mass of a friable yellow substance (" Pharaoh's Serpent ").

(4) A mixture of 5 gm. of clean fine iron filings and 3 gm. of flowers of sulphur is heated in a test-tube. The mixture glows and continues to do so when taken from the flame. The change evolves a good deal of heat. When cold, the tube is broken in a mortar. A greyish mass is obtained, which is easily powdered in the mortar. The powder is black, and under a lens no iron or sulphur particles can be seen in it, although these can be seen in the mixture. Carbon disulphide does not dissolve any sulphur from it (p. 2). If a magnet is brought over it iron is not attracted, as it is from the mixture.* The iron and sulphur have disappeared as such and have formed a new substance, a chemical compound, iron sulphide.

From these experiments it is seen that chemical changes are often accompanied by an evolution of heat. This is not always the case, since sometimes heat is absorbed.

(5) Concentrated hydrochloric acid is poured over crystals of Glauber's salt in a beaker; the crystals fall to a granular white powder of common salt and a considerable absorption of heat occurs, so that water in a small test-tube placed in the beaker is frozen.

Characteristics of physical and chemical changes.—Some of the main characteristics of physical and chemical changes may be summarised. It may be noted that the difference between chemical and physical changes is sometimes not very marked.

I. Physical changes : no new substance is produced : if anything more than mere heating or cooling is involved, it is usually merely a change of state (melting, evaporation) : apart from latent heat absorbed or evolved in changes of state, and heat supplied to or removed from a body, there is no marked evolution or absorption of heat : the change is easily reversed by appropriate alteration in the external conditions : the weight of the material remains unchanged.

II. Chemical changes : new substances with different properties are produced : there is usually evolution of heat (sometimes absorption of heat), and sometimes (as in combustion) of light : the change is not easily reversed by mere change of external conditions unless the system is in a state of equilibrium (see p. 49) : the weight of the material usually changes when it is converted into the new substance.

Gases usually require heating before they react chemically, and solids usually react only when fused or dissolved, although sometimes slight reaction occurs when fine powders are strongly compressed or are ground in a mortar.

* The powder is usually *feebly* magnetic as a whole. It may be noted as a curiosity that the composition of ferrous sulphide (nearly always given as the example of a chemical compound) is never exactly that given by the chemical formula FeS and is slightly variable ; it always contains a little less iron than the formula indicates.

The law of conservation of mass.—To show that the *total* weight is constant in a chemical change this must be carried out in a closed space, so that no material can escape.

A small piece of white phosphorus is cut from a stick of the material lying under water, is quickly dried between filter papers and placed by means of crucible tongs (*dry phosphorus must never be touched with the fingers*) in a strong dry 250 c.c. round-bottom flask, tightly closed by a rubber stopper. The flask is weighed. The phosphorus is warmed by a small flame till it ignites. When the combustion has ceased the flask is allowed to cool, and is reweighed. The weight is unchanged.

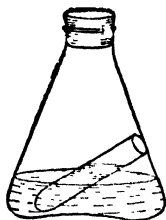


FIG. 12.—Chemical reaction in a closed space.

In another experiment, a little ferric chloride solution in a test-tube is placed inside a flask containing potassium ferrocyanide solution, and the flask corked and weighed (Fig. 12). On tilting the flask, the liquids mix and a deep-blue precipitate forms. There is no change in weight.

These and similar experiments show that *there is no change in total weight when a chemical reaction occurs*, so that the weight of the products of the reaction is equal to the weight of the substances which entered into reaction.

Weight is proportional to mass, which measures quantity of matter, hence the result is usually called the **law of conservation of mass**, or the **law of indestructibility of matter**. It was demonstrated with great accuracy in Landolt's experiments (1893-1908).

In the separate legs of a Jena glass U-tube (Fig. 13) he sealed solutions of substances capable of reacting without the production of much heat, so that the disturbances arising from this cause could be eliminated. He used :

1. Silver sulphate and ferrous sulphate, giving a precipitate of metallic silver.
2. Hydriodic acid and iodic acid, giving a precipitate of iodine.
3. Iodine and sodium sulphite, giving sodium iodide and sulphate.
4. Chloral hydrate and caustic potash, giving an emulsion of chloroform.

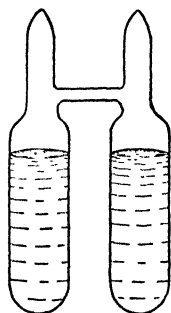


FIG. 13.—Landolt's experiment.

The tube was counterpoised against an exactly similar tube on a balance detecting a change of weight of 0.0001 gm. with a load of 1 kgm. in each pan, a change of 1 part in 10,000,000. One reaction tube was inverted and the chemical change allowed to take place. After cooling, the tube was replaced on the balance and the weight noted. The other tube was then taken off the balance and inverted and the process repeated.

At first slight diminutions in weight, 0.167 mgm. in the maximum, were always found, but after a long series of experiments these were traced to two causes, both due to the slight evolution of heat :

(a) the film of moisture condensed on the outer surface of the glass was partly driven off and did not return until after long standing ;

(b) the vessel expanded slightly and did not return to its original volume until after some time.

The first effect reduced the weight of the vessel, and the second effect, which led to an increase in the volume of air displaced by the vessel, also reduced the apparent weight. By allowing the vessel to stand for a long time before reweighing, Landolt found that it recovered its original weight to within 1 part in 10,000,000—*i.e.* within the limits of experimental error. By using silica tubes (which do not expand) covered with wax (to prevent the formation of a film of moisture) no change in weight was observed within the same limits of error. For these reactions, therefore, the law of conservation of mass is exact.

Very minute losses in weight are predicted by the Theory of Relativity for changes in which energy is evolved, but these are quite inappreciable in the chemical laboratory.

Elements and Compounds.—A substance may undergo a complete chemical change in one of two ways, according to its composition :

- (1) *The substance increases in weight in all changes, because it combines with other substances, or else the weight remains constant.**
- (2) *The substance decreases in weight in some changes, because it is decomposed into other substances.*

These results are found by experiments, of which the following are typical :

(1) Let 0.5 gm. of magnesium ribbon be heated in a weighed loosely covered porcelain crucible (Fig. 14) over a small flame till combustion ceases. Then heat strongly for ten minutes with the lid off, cool and weigh. There will be an *increase in weight* of a little over 0.3 gm. The magnesium has combined with oxygen from the air to form magnesium oxide : magnesium + oxygen = magnesium oxide.

(2) Let 2.16 gm. of red oxide of mercury (mercuric oxide) be placed in a weighed hard glass tube, and the tube connected by a rubber stopper with a glass delivery tube leading to a pneumatic trough in which is inverted a measuring cylinder full of water, the mouth supported on a beehive shelf over the delivery tube (Fig. 15). On heating the mercuric oxide, bubbles of gas collect in the cylinder. At the same time a shining metallic sublimate of mercury collects on the cooler part of

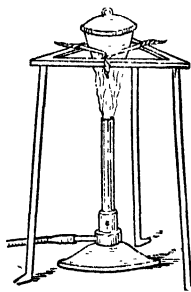


FIG. 14.—Heating magnesium in air.

* The weight remains constant in allotropic changes (p. 24), *e.g.* the change of white into red phosphorus.

the glass tube. When the evolution of gas ceases and the oxide has disappeared, the delivery tube is removed from the trough and the apparatus is allowed to cool. The tube is again weighed, and the *loss in weight* should be 0.16 gm. The volume of gas collected will be about 118 c.c. If a slip of wood which has been kindled and blown out is

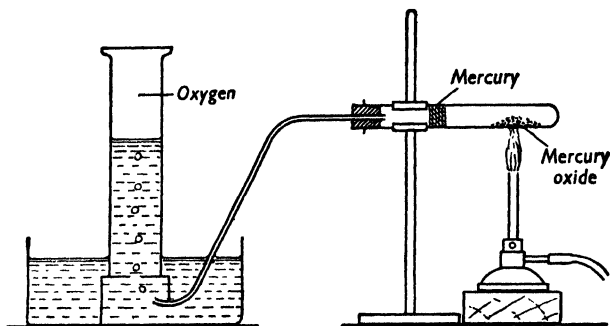


FIG. 15.—Heating mercuric oxide.

placed in the gas, the glowing tip is rekindled and the chip burns with a brilliant flame, indicating that the gas is oxygen. The mercuric oxide has decomposed into mercury and oxygen: mercuric oxide = mercury + oxygen. This experiment shows that 216 parts by weight of mercuric oxide contain 200 parts of mercury and 16 parts of oxygen.

If a *pure substance* can be decomposed into two or more substances each of smaller weight, as the red oxide of mercury into mercury and oxygen gas, we say that it is a *compound*. If it always yields substances of greater weight, showing that combination with other substances occurs, the substance is called an *element*. Magnesium is an element.

Note that we do not call *solutions* of salt and water, which may be separated into salt and water by mere evaporation, compounds. They are not *pure substances*.

The above definitions show the all-important part played by the balance in Chemistry, and it is clear also that they assume the correctness of the law of conservation of mass.

It is often said loosely that a substance is an element when it cannot be "split up" into "simpler" substances, but this is rather inadequate, since chemists do not go about their business with hatchets and it is not said how it is known that the products are "simpler". What is usually meant is that a substance is a compound if a known element can be obtained from it alone. Potassium chlorate gives off oxygen on heating, hence it must contain oxygen (an element) and must be a compound. Bearing all the implications in mind, it may be said that :

An element is a substance which cannot be decomposed by chemical methods into simpler substances.

This definition was clearly stated by Robert Boyle (1627-1691), who in his *Sceptical Chymist* * (1661) agrees to use "elements and principles as terms equivalent, and to understand both by the one and the other, those primitive and simple bodies of which the mixed ones are said to be composed, and into which they are ultimately resolved". According to Boyle, the elements are the practical limits of chemical analysis.



FIG. 16.—ROBERT BOYLE (1627-1691).

Lavoisier, in his *Traité de Chimie* (1789), adopted the same definition, at the same time emphasising that at some future date, with improved methods, substances then regarded as elements might be shown to be compounds, although "we ought never to suppose them compounded until experiment and observation have proved them to be so".

A list of the elements is given on the inside of the front cover and the physical properties of most of them in the table on p. 20. About 99 per

* Reprinted in the *Everyman* series.

cent. of terrestrial matter is composed of about twenty common elements, and the occurrence of the elements in the air, sea and crust of the earth to a depth of twenty-four miles is shown in Fig. 17.

Analysis and synthesis.—The process by which a compound is separated into its constituent elements, *e.g.* the decomposition of red oxide of mercury by heat, is called analysis, from the Greek *analuo*, I unloose. The building up of a compound from its elements, as in the production of magnesium oxide by heating magnesium in air, is called synthesis, from a Greek word meaning putting together.

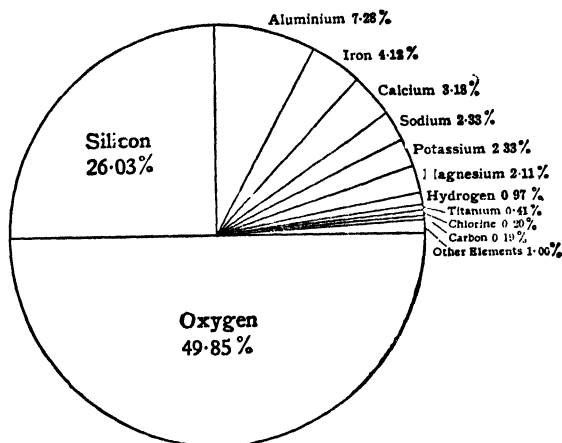


FIG. 17.—The distribution of the elements.

The law of constant proportions.—The composition of a *mechanical mixture* can obviously be varied at will, and that of a *solution* is also variable within certain limits. There is no reason why we should assume that the composition of a *pure compound* is always the same until this has been shown to be true by experiment. The way to do this is to prepare the same compound by as many different ways as possible and to show by analysis or synthesis that it always has the same composition. This may be illustrated by two experiments in the case of oxide of tin. Metallic tin may be converted into oxide in two ways, and the same weight of oxide of tin is obtained from 1 gm. of tin in both methods, hence the compound has the same composition.

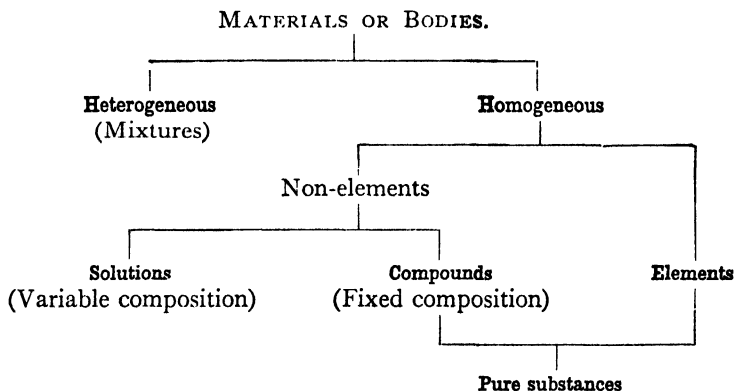
(1) 1 gm. of tin is heated in a weighed Rose's crucible (Fig. 18) * in a slow stream of oxygen until the weight becomes constant. Oxide of tin is formed.

* A clay tobacco-pipe with the bowl inverted in an ordinary porcelain crucible will serve instead.

(2) 1 gm. of tin is acted upon by concentrated nitric acid in a weighed porcelain basin (covering with a watch-glass to avoid loss by spirting) until it is converted into a white mass. The dish is then heated until the weight is constant. Oxide of tin is formed and its weight is the same as in experiment (1).

The point at issue is between a solution and a compound. A substance which is not an element but always has the same composition however it is prepared is called a **compound**. A homogeneous material which can vary in composition between certain limits is called a **solution**.

The arrangement in the following table summarises the contents of the preceding paragraphs :



As a result of a large number of analyses of compounds, both minerals occurring in nature and substances prepared in the laboratory, the French chemist Proust* at the end of the seventeenth century put forward the law of constant proportions :

Elements always combine in fixed ratios by weight, so that the composition of a pure chemical compound is always the same.

Another French chemist, Berthollet (1748-1822),* who accompanied Napoleon on his expedition to Egypt, called this result into question. He believed that the composition of a compound could vary, partly owing to differences in the method of preparation, so that he drew no distinction between compounds and solutions. Most of the examples which Berthollet brought forward were shown by Proust to be mixtures or solutions of two or more compounds, each of definite composition. Berthollet in his work arrived at an important law, called the law of mass action (see Chapter XIX), although he was wrong in his contention of the

* See Partington, *A Short History of Chemistry*, Chapter VIII.

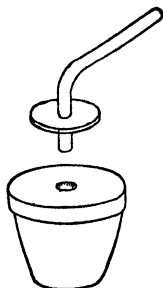


FIG. 18.—Rose's crucible.

MELTING AND BOILING POINTS OF THE CHEMICAL ELEMENTS (in degrees C.)

Element.	M. pt.	B. pt.	Element.	M. pt.	B. pt.	Element.	M. pt.	B. pt.
Aluminium	659.8	>2200	Iodine	113.9	184.4	Rhodium	1960	>2500
Antimony	630.5	1380	Iridium	2440	>4800	Rubidium	39.00	700
Argon	-189.2	-185.9	Iron	1539	2450	Ruthenium	2450	>2700
Arsenic	814.5*	subl. 615	Krypton	-157	-152.9	Samarium	1350	—
Barium	710	1536	Lanthanum	810	1800	Scandium	1200	2400
Beryllium	1280	1500	Lead	327.3	1620	Selenium (grey)	220	685
Bismuth	271	1450	Lithium	180	1336	Silicon	1420	2600
Boron	2300	2550	Magnesium	651	1100	Silver	960.8	1955
Bromine	-7.2	58.8	Manganese	1260	1900	Sodium	882.9	882.9
Cadmium	320.9	767.3	Mercury	-38.87	356.95	Strontium	800	1365
Caesium	28.45	670	Molybdenum	2620	3700	Sulphur	{S ₂ 112.8 S ₈ 119.25}	444.60
Calcium	851	1439	Neodymium	840?	—	Tantalum	2850	>4100
Carbon	3500	4200	Neon	-248.5	-245.9	Tellurium	449.8	1390
Cerium	640	1400	Nickel	1455	2900	Thallium	303.5	1475
Chlorine	-101.6	-34.5	Niobium	1950	3700	Thorium	1845	>3000
Chromium	1840	2200	Nitrogen	-210	-195.8	Tin	231.84	2260
Copper	1083.0	2310	Osmium	2750	>5300	Titanium	1725	>3000
Cobalt	1495	2900	Oxygen	-218.4	-183.0	Tungsten	3390	5900
Fluorine	-218	-187	Palladium	1552	2200	Uranium	1133	1500
Gallium	29.75	>2000	Phosphorus	44.1	287	Vanadium	1710	3000
Germanium	958	2700	Platinum	1769	4300	Xenon	-111.5	-107.1
Gold	1063.0	2610	Potassium	63.5	758	Yttrium	1475	2500
Hafnium	2200	3200	Praseodymium	940	—	Zinc	419.45	920
Helium	-272†	-268.87	Radium	960	1140	Zirconium	1600	>2900
Hydrogen	-259.14	-252.76	Rhenium	-71	-61.8			
Indium	155.4	2000		3167	—			

* At 36 atm.

† At 23 atm.

variability in composition of compounds. The law of constant proportions was fully recognised when the atomic theory was put forward, since it is a simple result of this theory (see Chapter VIII). It should be carefully noted that although a compound has a definite composition, there may be different compounds of the same composition ; these are called **isomers** (see p. 24).

Recent experiment has shown that the Law of Constant Proportions requires extension. An element such as lead or chlorine can exist in more than one modification, and the separate modifications called **isotopes** have different combining proportions. Since the common element as found in nature is nearly always a mixture of isotopes in an unvarying ratio, it behaves as a simple substance with a constant combining weight, but in some cases (*e.g.* the varieties of lead produced by radioactive changes) some variations in natural specimens have been found. This matter is more fully considered in Chapter XX.

Atomic weights and symbols of the elements.—The following is a list of some common elements, with their **symbols**, in some cases derived from the Latin (or Latinised) names. These **symbols** were first used by Berzelius in 1813. The numbers represent the **atomic weights** of the elements.

Every element is supposed, according to the atomic theory put forward by Dalton in 1803, to consist of exceedingly small particles called **atoms**, the atom of each element having a characteristic weight. If the atomic weight of hydrogen is taken as 1 the atom of oxygen, for example, is sixteen times as heavy as that of hydrogen.

The symbol of an element represents one atom, or one atomic weight, of the element.

Aluminium - - - Al	27	Iodine - - - I	127
Antimony (<i>Stibium</i>) - Sb	122	Iron (<i>Ferrum</i>) - - Fe	56
Argon - - - A	40	Lead (<i>Plumbum</i>) - - Pb	207
Arsenic - - - As	75	Magnesium - - - Mg	24
Barium - - - Ba	137	Manganese - - - Mn	55
Bismuth - - - Bi	209	Mercury (<i>Hydrargyrum</i>) Hg	201
Boron - - - B	11	Nitrogen - - - N	14
Bromine - - - Br	80	Oxygen - - - O	16
Calcium - - - Ca	40	Phosphorus - - - P	31
Carbon - - - C	12	Potassium (<i>Kalium</i>) - K	39
Chlorine - - - Cl	35.5	Silicon - - - Si	28
Chromium - - - Cr	52	Silver (<i>Argentum</i>) - Ag	108
Copper (<i>Cuprum</i>) - Cu	63	Sodium (<i>Natrium</i>) - Na	23
Fluorine - - - F	19	Sulphur - - - S	32
Gold (<i>Aurum</i>) - Au	197	Tin (<i>Stannum</i>) - Sn	119
Hydrogen - - - H	1	Zinc - - - Zn	65

Molecules and molecular weights.—The smallest particle of an element or compound which can exist in the *free* state is called a **molecule**. Although the molecules of a few elements, such as mercury vapour, contain only one atom, those of the common gases (oxygen, hydrogen, nitrogen, chlorine) contain **two**, and the molecules of phosphorus and arsenic contain four atoms. A molecule of a compound contains a fixed number of atoms of the elements, and in the **formula** of a compound the symbols of its elements are written with a small whole number *below* each to show how many atoms are present (the figure 1 being always understood). For example, the molecule of mercuric oxide contains one atom of mercury and one of oxygen and its formula is HgO ; a molecule of sulphuric acid contains two atoms of hydrogen, one atom of sulphur and four atoms of oxygen, and its formula is H_2SO_4 .

Since two elements may combine in more than one ratio, this is represented (1) by suffixes added to the Latin names, (2) by prefixes :

Cu_2O cuprous oxide	} Suffixes	SO_2 sulphur dioxide	} Prefixes
CuO cupric oxide		SO_3 sulphur trioxide	

The suffix *-ous* denotes the *lower*, and *-ic* the *higher*, proportion of an element (*e.g.* oxygen), respectively.

In a series of oxides the one containing the *highest* proportion of oxygen is sometimes called a *peroxide*, but it has been proposed to restrict this name to a special class of oxides, giving hydrogen peroxide (H_2O_2) with acids, such as sodium and barium peroxides, Na_2O_2 , BaO_2 . The name peroxide is used rather loosely, *e.g.* NO_2 , MnO_2 , and PbO_2 , which are not true peroxides, are sometimes called nitrogen, manganese, and lead "peroxides".

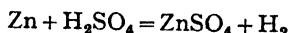
The formulae of salts containing water of crystallisation and of so-called "molecular compounds" and double salts are usually written with a comma separating the easily separated components, *e.g.* blue vitriol $\text{CuSO}_4, 5\text{H}_2\text{O}$ and alum $\text{K}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$. Sometimes a full-stop is used.

A mixture or solution has no formula, since it contains different kinds of molecules simply mixed together.

The **molecular weight** of a compound is the sum of the weights of the atoms present; *e.g.* the molecular weight of sulphuric acid is

$$(2 \times 1) + 32 + (4 \times 16) = 98.$$

A **chemical equation** is a method of representing a chemical reaction in terms of the atoms and molecules which take part in it. Thus :



means that one atom of zinc reacts with one molecule of sulphuric acid to produce one molecule of zinc sulphate and one molecule of hydrogen.

An equation must always show the same numbers of atoms on each side, or must be *balanced*. An equation has a meaning only when the reaction it represents can actually occur.

Types of chemical action.—It is usual to classify chemical changes into five groups or types :

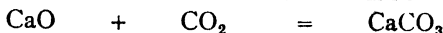
1. **Combination** : two or more elements combine to form a compound :

iron + sulphur = iron sulphide



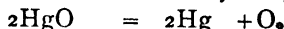
or two or more simple compounds combine to form a more complex compound :

calcium oxide + carbon dioxide = calcium carbonate



2. **Decomposition** : a compound decomposes into two or more elements or into simpler compounds :

mercuric oxide = mercury + oxygen



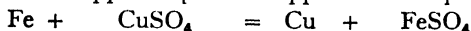
calcium carbonate \rightleftharpoons calcium oxide + carbon dioxide



When the change is *reversible*, as in the last example, the equals sign is replaced by \rightleftharpoons and the change is often called **dissociation**, which involves both combination and decomposition.

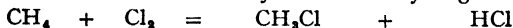
3. **Replacement** : one element replaces another in a compound :

iron + copper sulphate = copper + iron sulphate



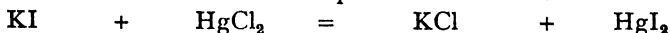
In reactions of carbon compounds, when an element or radical (p. 43) displaces another from a compound and at the same time the displaced element combines with another portion of the displacing element, the reaction is called **substitution** :

methane + chlorine = methyl chloride + hydrogen chloride



4. **Double decomposition** : two compounds react by exchange of parts to form two new compounds :

potassium iodide + mercuric chloride = potassium chloride + mercuric iodide

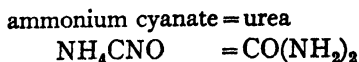


A type of double decomposition in which the compound is decomposed by water is called **hydrolysis** :

calcium sulphide + water = calcium hydroxide + hydrogen sulphide



5. **Isomeric change** : one substance changes into another having the same composition but different properties :

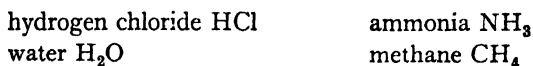


The existence of two or more substances having the same composition but different properties is called **isomerism**, and the different substances are called **isomers**.

Certain elements (*e.g.* carbon, sulphur and phosphorus) exist in different forms called **allotropes** ; the change from one form into another is called an **allotropic change**, and the existence of such forms is called **allotropy**. Some compounds can also exist in different modifications and the name allotropy is often used for this case also. Red mercuric iodide when rubbed on filter paper and heated changes into a yellow modification which remains yellow on cooling but becomes red again when rubbed with a glass rod. (Some substances change colour on heating, *e.g.* white zinc oxide becomes yellow, but the original colour is restored on cooling).

When an isomeric change is reversible it is often called a **tautomeric change**. When one allotropic form is stable above a certain temperature (*transition temperature*) and another below this temperature, the substance is called **enantiotropic** ; when only one form is stable at all temperatures the substance is called **monotropic**.

Valency.—Chlorine, oxygen, nitrogen, and carbon combine with hydrogen to form the compounds :



one atom of chlorine, oxygen, nitrogen and carbon combining with one, two, three and four atoms of hydrogen, respectively.

The number of atoms of hydrogen combining with one atom of an element measures what is called the **valency** of that element.

The valencies of chlorine, oxygen, nitrogen and carbon are one, two, three and four, respectively. Carbon and oxygen combine to form carbon dioxide CO₂, and since each carbon atom has four valencies and each oxygen atom two, the valencies of the carbon and oxygen in CO₂ both total four, and hence balance one another. Correct formulae may thus be written down by remembering the valencies of common elements.

CHAPTER III

THE COMPOSITION OF AIR AND THE THEORY OF COMBUSTION

The discovery of gases.—We can easily understand why the discovery of gases and the investigation of their properties were rather late in the study of Chemistry. Gases are not so easy to detect and study as liquids and solids. Van Helmont, who invented the name *gas* about 1630, had described two gases: *gas sylvestre* (carbon dioxide) and *gas pingue* (impure hydrogen or perhaps marsh gas), but he thought a gas could not be contained in a vessel. Robert Boyle about 1650 was probably the first to collect a gas. He filled a bottle with dilute sulphuric acid, put some iron nails in it, and inverted the bottle in a dish of the acid. Bubbles of gas (hydrogen, which he called a "factitious air") rose from the iron and collected in the bottle. Boyle also knew that hydrogen was inflammable.

In 1727 the Rev. Stephen Hales (1677-1761), vicar of Teddington in Middlesex, in his *Vegetable Staticks* described experiments on gases. He heated various materials in a bent iron gun-barrel and collected the gas evolved in a large globe inverted in a tub of water (Fig. 19). He obtained several gases but contented himself with measuring their volumes without studying their properties, and so missed the discovery of the individual gases.

Joseph Priestley (1733-1804), a nonconformist minister, published six volumes of *Observations on Different Kinds of Air*, the first appearing in 1774, in which he describes his discovery of several gases. Henry Cavendish (1731-1810) in 1766 had published some very careful experiments on two gases then known; carbon dioxide, which was called *fixed air* (discovered by Black in 1755) and hydrogen (called *inflammable air*, and known to Boyle). Priestley, in addition to collecting gases over water in the pneumatic trough, showed that those which are very soluble in water, such as ammonia gas and sulphur dioxide, may be collected over mercury. (Cavendish was the first to collect a gas over mercury.*)

* On Black's, Cavendish's and Priestley's work, see Partington, *A Short History of Chemistry*, Chapter VI, and *Alembic Club Reprints* Nos. 1, 3 and 7.

The calcination of metals.—The metals, except gold, silver and platinum, when heated in open crucibles, form a cross which was called a *calx* (Latin *calx*, lime). It was noticed in the sixteenth century that this *calx* is heavier than the metal. The experiment may be carried out by heating a weighed quantity of tin or lead in an open crucible.

Jean Rey in 1630 mentions the increase in weight of tin on calcination and suspected that it was due to air which had become thicker on heating

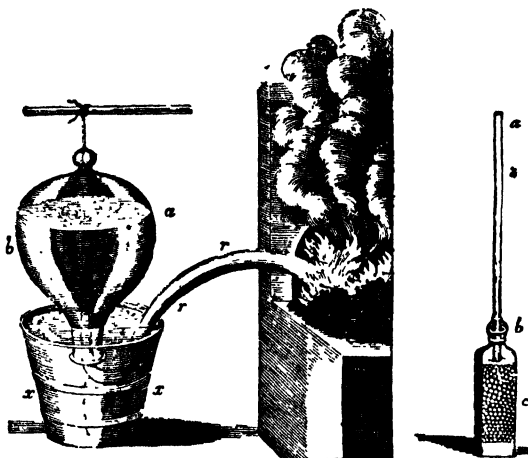


FIG. 19.—Apparatus used by Hales.

On the left is the gun-barrel (*r*) heated in a fire. The gas is collected in the globe (*ab*) over water in the tub (*xx*). On the right is a bottle filled with fermenting peas over mercury. The pressure of the gas evolved drives the mercury into the vertical tube (*ab*), which is firmly fixed into the bottle and dips into the mercury in the lower part.

and had adhered to the *calx** (not the *metal*). He was clear that air had weight.

This increase of weight is readily shown by an experiment. Some finely divided *reduced iron* is taken up by a horse-shoe magnet, hung from one arm of a balance, a piece of asbestos paper being placed in the pan underneath the magnet. A spirit-lamp flame is applied to the tufts of iron adhering to the magnet; the powder begins to glow and after calcination falls from the magnet. The pan on the same side of the balance as the magnet sinks, showing that the iron increases in weight on calcination.

The phlogiston theory.—A theory put forward by Stahl† about 1700 assumed that when bodies burn or are calcined something called *phlogiston*

* See *Alembic Club Reprint* No. 11.

† George Ernst Stahl (1660-1734) was professor at Halle and later physician to the King of Prussia in Berlin. He developed the ideas put forward in 1669 by Johann Joachim Becher (1635-1682), whose *terra pinguis* he named phlogiston.

(from the Greek, *phlox* = flame) escapes. Oil, wax, and charcoal, which are all combustible bodies, are rich in phlogiston and may be used to restore it to a burnt material from which it has escaped. Zinc on heating to redness burns with a brilliant flame, hence phlogiston (which may be represented by the Greek letter Phi, ϕ) escapes. The white residue is calx of zinc : $\text{zinc} = \text{calx of zinc} + \phi$. If it is heated with charcoal (rich in phlogiston) the calx is reduced and zinc distils. Hence : $\text{calx of zinc} + \phi = \text{zinc}$. Similarly with other metals. If phosphorus is burnt it produces an acid matter and much heat and light are evolved. Hence : $\text{phosphorus} = \text{acid} + \phi$. If the acid is heated with charcoal, phlogiston is absorbed and phosphorus distils.

During the eighteenth century when this theory was held, the increase in weight of metals on calcination was usually ignored, although the fact was destined to overturn the whole theory of phlogiston when attention was paid to the *quantitative* aspect of chemical changes by Lavoisier (p. 31).

Although the assumption that a burning body unites with part of the air will explain the results of experiments on combustion, on the calcination of magnesium (p. 15) and of iron, it was necessary in order to disprove the phlogiston theory to prepare this constituent of the air and to show that it really does unite with substances when these are burnt or calcined.

A clue had been provided by some experiments made by Robert Hooke (1635-1703) in 1665, and especially in the experiments of John Mayow (1641-1679) and the explanation he gave of them.

The experiments of Hooke and Mayow.—Hooke found that a bit of charcoal or sulphur burns brilliantly when thrown into fused nitre (saltpetre).

If small quantities of nitre are fused in two hard glass test-tubes or porcelain crucibles, and small fragments of charcoal and sulphur thrown into them, the charcoal swims about burning brightly and the sulphur burns with a beautiful blue flame.

Hooke assumed * that there is a gas present in common air which is also contained in a fixed state in nitre (saltpetre) ; this gas he later called "nitrous air"†, and since bodies burn more vigorously in fused nitre than in air, there is more nitre air in the nitre than in the air.

John Mayow in 1674‡ published a theory and new experiments. He concluded that air consists of two gases ; one is nitre air, called by

* In his *Micrographia*, 1665 ; extracts in *Alembic Club Reprint* No. 5.

† Since this name was later used by Priestley for another gas (nitric oxide), the name "nitre air" will be used in what follows.

‡ In his *Tractatus Quinque Medico-Physici*, translated in full in *Alembic Club Reprint* No. 17. The work is not described in his earlier *Tractatus Duo* in 1668.

conveniently performed with the apparatus of Fig. 23. The tap must be turned off as soon as the flame (which becomes very faint) goes out.

Scheele was able to prepare pure fire air by heating nitre and also oxide of mercury. He found it to be a colourless gas which supports

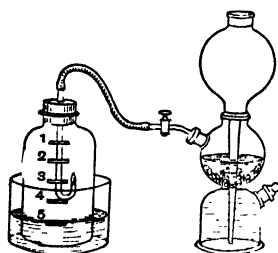


FIG. 23.—Combustion of hydrogen in air.

combustion much better than common air and is *completely* absorbed by moist liver of sulphur. When he burnt phosphorus in a flask of it, the cork could not be taken out under water but could be pushed in, when water rushed in and filled the flask. A hydrogen flame continued burning in the gas until practically all was absorbed.

Scheele also proved that fire air is *completely* absorbed by the respiration of bees.

When fire air was added to foul air left after combustion of hydrogen etc. in air, so as to restore the original volume, the mixture had all the properties of ordinary air, *e.g.* it left the same residuc after standing over liver of sulphur.

If four-fifths of a gas-jar, divided into 5 parts, are filled with nitrogen ("foul air") and then the remaining fifth is filled with oxygen ("fire air"), no heat is evolved, and a taper burns in the mixture exactly as it does in common air. The taper is extinguished in the nitrogen alone and burns with great brilliancy in oxygen.

Scheele thus proved the part played by fire air (oxygen) in both combustion and respiration, and so completed the work of Mayow.

Priestley's experiment.—Whilst Scheele was carrying out his experiments in Sweden, Priestley in England was also busy with experiments on gases.* He tried to extract "air" from a miscellaneous collection of chemicals which happened to include oxide of mercury, which was then called red precipitate or *mercurius calcinatus per se*, and was obtained by heating mercury in air. The substances were heated by focusing the sun's rays on them in small phials filled with and inverted over mercury. Priestley says :

"Having procured a lens of twelve inches diameter, and twenty inches focal distance, I proceeded with great alacrity to examine, by the help of it, what kind of air a great variety of substances, natural and factitious [*i.e. artificially prepared*], would yield. . . . With this apparatus, after a variety of other experiments, . . . on the 1st August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*; and I presently found

* The isolation of oxygen is described in his *Experiments and Observations on Air*, vol. ii. 1775; extracts in *Alembic Club Reprint* No. 7. He had obtained oxygen in 1772 by heating nitre but failed to distinguish it from air. Many of Priestley's experiments are suitable for repetition in a school laboratory and some are given in the author's *School Course of Chemistry*.

that, by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was, that a candle burned in this air with a remarkably vigorous flame."

Priestley had, of course, independently discovered Scheele's fire air; he called the gas *dephlogisticated air*, since he thought combustion ceased



FIG. 24.—A. L. LAVOISIER (1743-1794)

when a given volume of air was saturated with phlogiston emitted from a burning body, and since the new "air" supported combustion much better than common air, it contained less phlogiston than this.

Lavoisier's experiment.—In October 1774 Priestley was in Paris and told Lavoisier of his discovery. Lavoisier was soon able to give the correct explanation of all these experiments. He recognised that metallic mercury when converted into red precipitate by heating in air combined with part of the latter, leaving the other gas (Scheele's "foul air"), and when the resulting red precipitate was strongly heated it

decomposed into its constituents, mercury and "pure air". He was able to prove that it is this "pure air" (or dephlogisticated air) which is absorbed in the calcination of metals, by a famous experiment described in his *Traité de Chimie*, 1789.*

He heated 4 oz. of mercury in a retort which communicated with a measured volume of air in a bell-jar over mercury (Fig. 25). The volume of air in the bell and in the retort was 50 cu. in. After a time red specks and scales of calx formed on the surface of the mercury. After twelve days the scales no longer increased; the fire was removed and the experiment stopped. The air had contracted to 42 cu. in., and the gas left was a "mephitic air",† which Lavoisier afterwards called "azote"; Chaptal called it "nitrogen" in 1790. The scales of mercury calx were

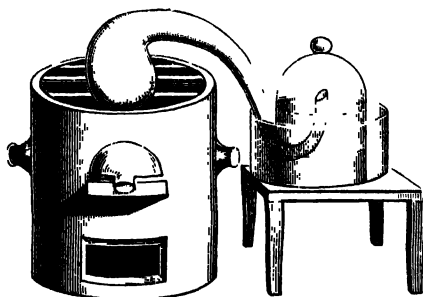


FIG. 25.—Lavoisier's apparatus.

collected and found to weigh 45 grains. They were heated in a small retort and gave off 8 cu. in. of "an elastic fluid much more capable of supporting respiration and combustion than ordinary air", and hence at first called by Lavoisier "vital air", or "air eminently respirable", and 41½ grains of mercury were left in the retort. When this vital air was added to the atmospheric nitrogen, ordinary air was formed without any evolution of heat or light, hence air is probably simply a mixture of these two gases (as had previously been suggested by Scheele) and not a compound.

Combustion in oxygen.—Lavoisier found that when the non-metals sulphur, phosphorus and charcoal burn in vital air they produce acidic oxides, forming with water acids which turn blue litmus red, and hence he called the gas *oxygen*, from two Greek words meaning "producer of acid". Metals when heated in it formed basic oxides (*calces*).

After the isolation of oxygen and the proof that it unites with combustible or oxidisable bodies during combustion or calcination, the

* Abridged edition, in a volume of *Les classiques de la découverte scientifique*, Gauthier-Villars, Paris,

† *Mephitis*, a noxious exhalation from the ground, Vergil, *Aeneid*, vii. 84; Lavoisier's name is "mofette".

phlogiston theory was not only unnecessary but also incorrect, since combustion was not due to the *loss* of anything by a burning body but to the *gain* of oxygen.

The increase in weight when phosphorus burns may be shown by the following experiment. A small piece of dry phosphorus is placed between

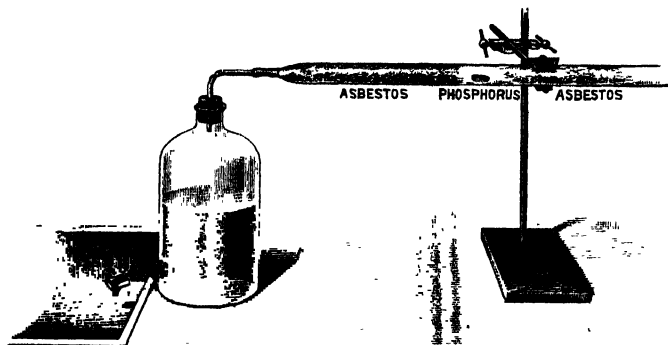


FIG. 26.—The oxidation of phosphorus.

two plugs of asbestos in a glass tube (Fig. 26) and the tube weighed. It is attached to an aspirator bottle from which a slow stream of water is allowed to run, thus causing a current of air to pass through the tube. The tube is heated gently until the phosphorus takes fire. The white fumes produced in the combustion are mostly retained by the asbestos. When combustion ceases, the tube is allowed to cool and weighed. It will have gained in weight.

CHAPTER IV

THE COMPOSITION OF WATER

The combustion of hydrogen.—Macquer in 1776-7 noticed that drops of water are deposited on a cold porcelain saucer “licked” by a hydrogen flame, but he paid no further attention to the result. The experiment is more conveniently made as follows.

A jet of hydrogen gas, obtained from zinc and dilute sulphuric acid in a flask (see p. 129) and dried by passing over calcium chloride (see p. 63), is burnt under a round-bottom flask through which cold water is circulated (Fig. 27). *Care must be taken that all the air is displaced*

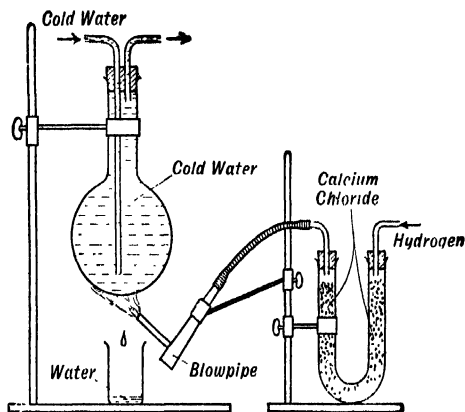


FIG. 27.—Formation of water by the combustion of hydrogen in air.

from the flask before the hydrogen flame is kindled, otherwise an explosion will occur : the gas is first tested as described on p. 131. Since the end of a glass tube may fuse together at the temperature of the flame, it is convenient to use a Black's blowpipe as shown.

Drops of liquid collect on the outside of the cold flask and may be received in a beaker. The liquid is easily recognised as water : (i) it is odourless ; (ii) it has no distinctive taste ; (iii) it has no action on litmus paper ; (iv) it turns anhydrous copper sulphate blue (p. 9) ; (v) if a sufficient amount is collected the boiling point may be determined in a test-tube fitted with a cork carrying a thermometer and a short outlet tube, and will be found to be 100° .

This experiment shows that *water is formed by the combustion of hydrogen in air.*

Scheele's experiment (p. 29) proved that hydrogen on combustion in air removes only the oxygen and is extinguished in the residual nitrogen. Hence *water is formed by the combustion of hydrogen in oxygen*. This is proved directly in the following experiments.

The explosion of a mixture of hydrogen and oxygen.—If the oxygen necessary for the combustion of hydrogen is first mixed with the gas and the mixture kindled, a very rapid combustion occurs, accompanied by a loud explosion.

The mixture is made in a *strong* soda-water bottle wrapped in a towel and put in an iron mortar, and a lighted taper brought to the mouth (after removing the cork).*

The explosion of a mixture of hydrogen (*inflammable air*) and oxygen (*dephlogisticated air*) when kindled was observed in 1781 by Priestley, who also noticed that a "dew" was formed on the inside of the vessel.

In order to examine the product of the reaction it is necessary to explode the gas mixture in a very strong *closed* vessel in which it is most conveniently kindled by an electric spark passed between two platinum wires sealed through the glass and connected with an induction coil. Very little noise is heard, usually a dull thud or sometimes a sharp click, according to the apparatus used.

Cavendish's experiments.—Cavendish (who knew of Priestley's experiment) in 1781 kindled a mixture of common air and inflammable air (hydrogen) in a strong glass globe by means of an electric spark † (Fig. 28). He found that with a little over 400 vols. of inflammable air to 1000 vols. of common air, "almost all the inflammable air and about one-fifth part of the common air, lose their elasticity, and are condensed into the dew which lines the glass". There was no change in weight after explosion. Since air contains



FIG. 28.—Cavendish's firing globe ("eudiometer").

* It is always wise to take all precautions against injury caused by the bursting of glass vessels in explosion experiments, especially in demonstrations when other persons are present. It is foolish to explode the mixture in a gas-jar.

† See *Alembic Club Reprint* No. 3; Cavendish's experiments were published in 1784; see also Partington, *The Composition of Water*, Bell and Sons, 1928. The student should notice the distinction between kindling an explosive mixture by a *single* spark and the combination of nitrogen and oxygen gases (p. 475), or the decomposition of a gas like ammonia (p. 470), by *prolonged* sparking.

about one-fifth its volume of oxygen, about 400 vols. of inflammable air will have combined with 200 vols. of oxygen, or the ratio of the combining volumes of hydrogen and oxygen is 2 to 1.

To examine the nature of the dew, Cavendish performed an experiment similar to that described on p. 34, in which a jet of hydrogen was burnt inside a long glass tube closed at one end. The product was water.

Cavendish now kindled a mixture of dephlogisticated air (oxygen) and inflammable air (hydrogen) in the firing-globe by means of an electric spark. The gas "lost its elasticity" and on opening the stopcock the globe was again filled with the gas, admitted through a glass siphon from a jar, which took the place of that converted into liquid water by the explosion. In this way many successive explosions could be made.

Cavendish found that *2 vols. of hydrogen combine with 1 vol. of oxygen to form water*, although this explanation of his results was first clearly stated by Lavoisier. With pure oxygen and hydrogen there is no gaseous residue and the water formed is pure. Cavendish showed that the weight of water is equal to the weights of the gases. Cavendish's experiment is a proof of the composition of water by synthesis.

Synthesis of water in the eudiometer.—Bunsen's eudiometer (Fig. 29) * consists of a strong glass tube sealed at one end and provided with two

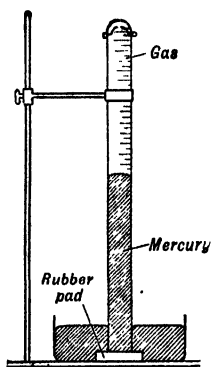


FIG. 29.—Bunsen's eudiometer, for exploding a mixture of gases confined over mercury.

platinum wires sealed through the glass for the purpose of passing an electric spark. It is graduated almost to the open end in mm. which are taken as measuring the volumes, since except at the closed end the cross-section is constant.

The eudiometer is filled with mercury and inverted over mercury in a trough. Pure hydrogen is passed in and the volume accurately read off, the corrections for temperature and pressure (see Chapter VII) being applied, the distance of the mercury meniscus in the tube from the level in the trough being subtracted from the barometer reading. A volume of pure oxygen rather less than a quarter that of the hydrogen is then added.†

The open end of the eudiometer is held down firmly on a pad of rubber beneath the mercury and an electric spark from a coil is passed. There is a flash of light in the tube and a dull noise is heard. Dew appears on the walls of the tube after cooling.

The eudiometer after cooling is lifted from the rubber pad and the volume of moist hydrogen remaining is read off and corrected for tempera-

* A more convenient but more complicated and expensive apparatus is described on p. 463.

† The explosion is less violent than with a 2 : 1 mixture

ture and pressure. It will be found that the two gases have combined in the ratio of 2 volumes of hydrogen to 1 volume of oxygen. That the residual gas is hydrogen may be confirmed by testing it with a taper.

The volume composition of steam.—In order to find *the volume of steam* produced from the combination of the gases, if it were kept gaseous, it is convenient to use a U-shaped eudiometer, the closed limb of which is surrounded by a glass jacket through which the vapour of boiling amyl alcohol (132°) is passed. The water produced by the explosion is then kept in the form of vapour (Fig. 30).

Twenty c.c. of hydrogen and 10 c.c. of oxygen are introduced, measured at the temperature of the jacket with the mercury levels adjusted to equality on both sides. The open end of the U-tube is firmly closed by a rubber stopper, and a spark passed from the coil. There is a flash of light and an immediate contraction. By taking out the stopper and running mercury into the open limb until the levels are again equal, it will be seen that the steam occupies 20 c.c. Hence

2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of steam.

If the *densities* of oxygen and hydrogen gases are known the experiment will enable us to calculate the composition of water by weight.

The density of oxygen at S.T.P. is 1.429 gm. per litre, that of hydrogen is 0.09 gm. per litre. The weight of two litres of hydrogen is 0.18 gm., and this combines with 1 litre, or 1.429 gm., of oxygen. Hence the weight of oxygen combining with 1 gm. of hydrogen to form water is accurately $1.429/0.18 = 7.94$ gm.

Lavoisier's analysis of water.—Lavoisier had been puzzled by the combustion of hydrogen in oxygen, which he thought, on the basis of his theory (p. 32) should form an acid. In 1783 he resolved to make the experiment of burning hydrogen in oxygen on a larger scale, so that the product should not escape his notice. In May or June of that year, however, Sir Charles Blagden told Lavoisier of Cavendish's experiments, and the French chemist was able to repeat and explain them. He said: "water is nothing but oxygenated hydrogen, or the immediate product of the combustion of oxygen gas with hydrogen gas".* As a neutral substance, it was an exception to his rule that non-metals form acidic oxides on combustion.

* Cavendish explained his results in terms of the phlogiston theory. Blagden was Cavendish's assistant.

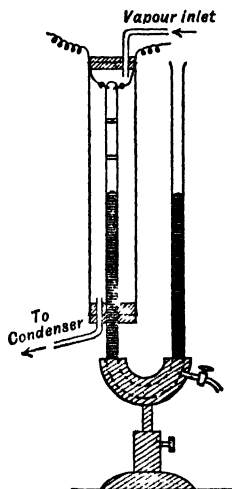
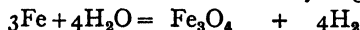


FIG. 30.—Volume composition of steam.

Lavoisier then tried to prove the composition of water by analysis (p. 18) but at that time it was possible to separate only the hydrogen from water, the oxygen combining with a metal to form an oxide, *e.g.* with iron :

iron + water = iron oxide + hydrogen



In 1784 he decomposed water by iron borings heated to redness in a gun-barrel.* Hydrogen was liberated and the iron converted into the black oxide formed when iron burns in oxygen. The experiment may be carried out as follows.

A piece of *weldless* iron pipe loosely packed with coarse iron filings or small iron nails is heated to redness in a combustion furnace (Fig. 31)

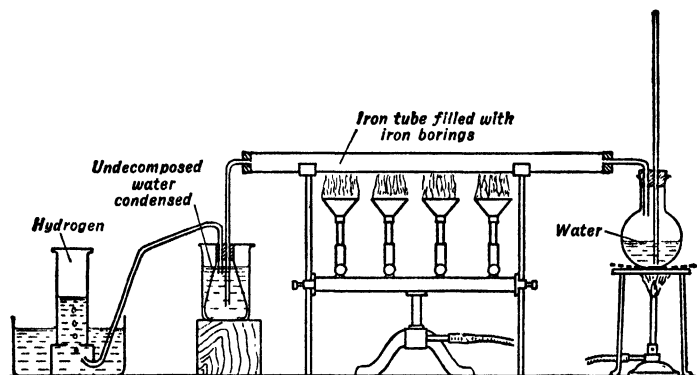
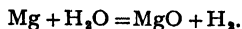


FIG. 31.—Decomposition of steam by red-hot iron.

and connected with a flask of water at one end and an empty cooled flask and gas delivery tube at the other. The water in the flask is boiled. Water collects in the empty flask, showing that the decomposition is not complete, but bubbles of gas are evolved from the delivery tube which may be collected in a jar and shown to be hydrogen.

The decomposition of steam is more easily shown by inserting with crucible tongs a piece of burning magnesium ribbon into a large conical flask in which water is boiling vigorously. The metal burns brightly in the steam and the hydrogen produced burns with a pale flame when kindled at the mouth of the flask ; white magnesium oxide is left :



The electrolysis of water.—The decomposition of water into hydrogen and oxygen by an electric current from a Volta's pile was discovered by Nicholson and Carlisle in 1800 and confirmed by Cruickshank in the same year ; Davy in 1806 showed that when very pure water is electrolysed, hydrogen and oxygen are the sole products. An apparatus for

* *Traité*, abridged (see p. 32), p. 50 f.

the decomposition, or *electrolysis*, of water by the electric current is shown in Fig. 32. It is called a *voltameter* (or better—as it measures coulombs not volts—a *coulometer*). It consists of two glass tubes with stopcocks, connected by a horizontal tube carrying a funnel for filling the apparatus with very dilute sulphuric acid. Pure water is almost a non-conductor of electricity but it allows the current to pass freely when a little acid is added, which conducts the current through the solution. Only the water is decomposed. The *electrodes* for leading the current into and out of the liquid consist of pieces of platinum foil and are connected with the positive and negative poles of a battery.

Bubbles of gas rise from each electrode; that coming from the positive wire occupies half the volume of the other gas, and if allowed to escape from the tap on to a glowing chip of wood it will rekindle the latter. This gas is oxygen. The gas evolved from the negative wire burns when kindled by a taper and is hydrogen.

Thus: *water is decomposed by electrolysis into 2 volumes of hydrogen + 1 volume of oxygen.*

The further study of the composition of water is taken up in Chapter XIII.

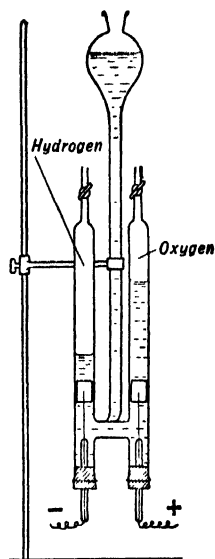


FIG. 32.—Decomposition of water by electrolysis.

CHAPTER V

ACIDS, BASES AND SALTS

General properties of acids and bases.—One of the objects of Chemistry is to arrange substances into groups of substances which have certain properties in common. Three important groups are **acids, bases and salts**.

Common acids met with in the laboratory are sulphuric, hydrochloric and nitric; and caustic soda, caustic potash, ammonia and lime are common examples of bases. The best known salt is common salt, but others such as nitre (or saltpetre), Glauber's salt (sodium sulphate) and Epsom salt (magnesium sulphate) are well known. Soda, potash and ammonia are examples of **alkalis**; all alkalis are bases, but there are bases such as lime which are not alkalis.

Since acids, alkalis and salts are easily differentiated by their common properties they were recognised as three groups of substances fairly early in the study of Chemistry.

Boyle in his *Experimental History of Colours* (1664) recognised the following **general properties of acids** :

- (1) They have a sour taste.
- (2) They act as solvents but with varying power on different bodies; the varying strength of acids was recognised by Tachenius in 1666.
- (3) They precipitate sulphur from a solution of liver of sulphur (poly-sulphides of potassium).
- (4) They turn red many blue vegetable colours (*e.g.* litmus), the colour being restored by alkalis.
- (5) They react with alkalis, the characteristic properties of each substance disappearing and a neutral salt being formed.

On the basis of these tests, Hoffman (1723) and Black (1755) were able to show that carbonic acid is a true acid, though a weak one.

(6) Cavendish in 1766 showed that hydrogen gas is evolved by the action of sulphuric and hydrochloric acids on zinc, iron and tin.

Examples of alkaline substances, viz. slaked lime, plant and wood ashes and *natron* (native sodium carbonate found in Egyptian lakes) were known to the ancients. Pliny mentions the *caustification* of alkalis by boiling with quicklime as known in Egypt. The alchemists were

acquainted with ammonium carbonate in the form of *spirit of hartshorn*, prepared by the destructive distillation of horn and bones or the putrefaction of urine. Later the names *mild alkali* and *caustic alkali* were introduced for the alkali before and after treatment with quicklime.

As **general properties of alkalis** the following were recognised :

(1) Their solutions feel soapy when rubbed between the fingers. (This is probably due to corrosion of the skin.)

(2) They restore the blue colour of litmus reddened by acids and turn juice of violets green.

(3) They neutralise acids to form salts.

(4) The "mild" varieties effervesce with acids, giving off a gas which was investigated by Black in 1755 and called by him "fixed air" (carbon dioxide).

Potash and soda were distinguished from one another by Duhamel in 1736 and by Marggraf in 1757.

Neutralisation.—When solutions of an acid and an alkali are mixed in the correct proportions the resulting solution has no acid taste, does not feel soapy and does not markedly change the colour of blue or red litmus, a purple colour being stable to the solution. On evaporation the solution gives a solid salt. This reaction is called **neutralisation** because the product has neither acid nor alkaline properties (Latin, *neuter*, neither). When caustic soda and hydrochloric acid are used the product is common salt; caustic potash and nitric acid form nitre; other salts can be prepared from the appropriate acids and alkalis or bases.

Neutralisation is an example of the quantitative aspect of Chemistry; only fixed amounts of acid and alkali will react to form a salt and if other amounts are used some acid or alkali is left over. Acids and alkalis react in fixed ratios and experiments show that these ratios are not the same for different acids and bases.

The names of acids, bases and salts.—Some acids, *e.g.* hydrochloric acid HCl , do not contain oxygen, and the names of their salts end in *-ide*, *e.g.* sodium chloride, potassium cyanide (NaCl , KCN). Many acids contain oxygen and are called **oxyacids**, *e.g.* sulphuric acid H_2SO_4 and nitric acid HNO_3 . All acids contain hydrogen. The terminations *-ous* and *-ic* are used to distinguish oxyacids containing less or more oxygen combined with the same elements, the terminations *-ite* and *-ate* being used for the corresponding salts :

ACID.	SALT.
Sulphurous H_2SO_3 .	Sodium sulphite Na_2SO_3 .
Sulphuric H_2SO_4 .	Copper sulphate CuSO_4 .
Nitrous HNO_2 .	Potassium nitrite KNO_2 .
Nitric HNO_3 .	Lead nitrate $\text{Pb}(\text{NO}_3)_2$.

Oxides forming acids with water are called **acidic oxides**, or sometimes **acid anhydrides** (Greek, *a* without, *hudo* water).*

SO₂ sulphurous anhydride.

SO₃ sulphuric anhydride.

P₂O₃ phosphorous anhydride.

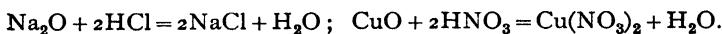
P₂O₅ phosphoric anhydride.

N₂O₃ nitrous anhydride.

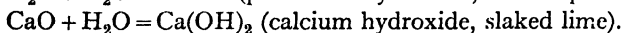
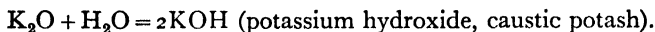
N₂O₅ nitric anhydride.

The acid anhydrides are now practically always called by their systematic names, *e.g.* sulphur dioxide (SO₂), nitrogen pentoxide (N₂O₅), etc.

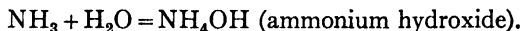
Oxides reacting with acids to form salts and water are called **basic oxides**. *E.g.* sodium oxide Na₂O, and copper oxide CuO :



By the combination of *some* basic oxides with water, **bases** are produced. These contain a metal (or radical, *cf.* below) united with a group of atoms OH called **hydroxyl**, and are therefore called **hydroxides** (not "hydrates" ; p. 8). Hydroxides of sodium and potassium are called *alkalis* ; the *oxides* of calcium, strontium and barium were formerly called *alkaline earths*.



We may suppose that ammonium hydroxide is formed when ammonia gas dissolves in water, since the liquid is alkaline :

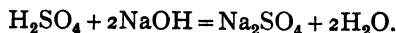


Acidic and basic oxides *combine* to form **salts** :



In the old *Dualistic System* of Berzelius salts were regarded as containing the basic and acidic oxides, called "electropositive" and "electro-negative" respectively, and formulated accordingly : sulphate of soda $\text{Na}_2\text{O}.\text{SO}_3$. This notation still has its uses in balancing equations of oxidation reactions, potassium permanganate being written K₂O.Mn₂O₇, and potassium dichromate K₂O.2CrO₃ ; ferrous sulphate FeO.SO₃ and ferric sulphate Fe₂O₃.3SO₃.

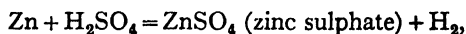
Acids and bases *react* to produce salts but water is formed at the same time :



The salt Na₂SO₄ may be regarded as sulphuric acid H₂SO₄ in which two atoms of hydrogen are replaced by two atoms of sodium. Thus acids

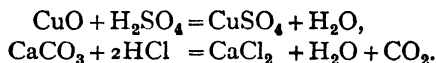
* The distinction between an "anhydride" and an "anhydrous substance" (p. 7) should be noticed.

may be considered as salts of hydrogen, which hydrogen can be displaced by metals. This may take place directly, for example when metallic zinc dissolves in dilute sulphuric acid :



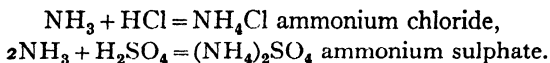
or indirectly when the acid is neutralised by a base.

Salts are also formed by the action of acids on basic oxides, hydroxides (bases) and carbonates ; with carbonates gaseous carbon dioxide is evolved with effervescence :



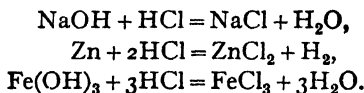
Besides *acidic* and *basic oxides*, *neutral oxides* (not forming acids or bases with water, *e.g.* nitric oxide NO, and carbon monoxide CO), *amphoteric oxides* (behaving at the same time as weak acids and weak bases, *e.g.* aluminium oxide), *peroxides* (higher oxides, containing much oxygen, see p. 146) and *double oxides* (composed of two oxides, *e.g.* ferrosferic oxide composed of ferrous oxide and ferric oxide : $\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$) are recognised.

Radicals.—Sometimes a *group of atoms* plays the part of a single atom and occurs in a whole series of compounds. Thus the salts formed by the combination of ammonia NH_3 with acids all contain the group NH_4 , which plays the part of the metal in other salts and is called ammonium :



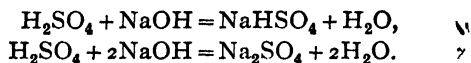
An unvarying group of atoms present in a series of closely related compounds is called a radical (Latin, *radix*, a root). The group OH (hydroxyl) in bases (hydroxides), the group SO_4 in sulphuric acid and sulphates, and the group NO_3 in nitric acid and nitrates, are radicals.*

Normal, acid, and basic salts.—When the molecule of an acid contains only one atom of hydrogen which can be replaced by a metal it can form only one class of salts. Thus hydrochloric acid can form chlorides in which *all* the hydrogen has been replaced by a metal. *An acid containing in its molecule only one atom of hydrogen which can be replaced by metals to form salts is called a monobasic acid :*



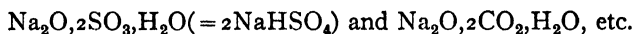
* In qualitative analysis the constituents of salts, viz. metals and ammonium and acid radicals, are often called "radicals" ; a mixture of calcium phosphate and ammonium sulphate "contains four radicals".

An acid containing in its molecule two atoms of hydrogen which can be replaced by metals and can form two classes of salts is called a dibasic acid. Sulphuric acid H_2SO_4 is dibasic. Either one atom of hydrogen can be replaced by a metal to form an **acid salt** or both atoms can be replaced to form a **normal salt** :



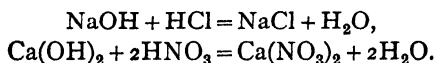
A normal salt is formed when all the acidic hydrogen of an acid is replaced by a metal (or ammonium). The names sodium hydrogen sulphate, etc., are now generally used instead of acid sodium sulphate, etc.

It must be remembered that an acid salt is not necessarily acid to litmus : sodium hydrogen carbonate NaHCO_3 , derived from the very weak carbonic acid H_2CO_3 , is alkaline to litmus. The name "normal" is practically never used in speaking of salts individually : we say simply "sodium sulphate", etc. Sometimes acid salts, besides being called sodium *hydrogen* sulphate, sodium *hydrogen* carbonate, etc., are called *bisulphate*, *bicarbonate*, etc., from the old formulae :

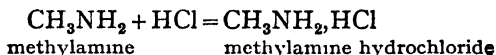


A base containing in its molecule one, two, etc., hydroxyl radicals which it loses on reaction with an acid to form salts is called a monacid, diacid, etc., base.

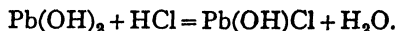
Caustic soda is a monacid base, calcium hydroxide is a diacid base :



These names are used also for organic bases which combine directly (like ammonia) with acids to form salts :

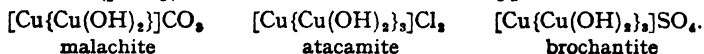


Basic salts may be regarded from two points of view. All bases contain hydroxyl OH, which reacts with the acidic hydrogen of acids to form water, and the other atom or radical of the base then forms a salt with the radical of the acid. When a base contains more than one hydroxyl group a salt can be formed which still contains one or more hydroxyl groups of the base :



We call Pb(OH)Cl **lead hydroxychloride** or basic lead chloride. Basic salts rarely have such simple formulae as this, and it is usual to regard them as compounds of normal salts with the free base or basic oxide. Thus the common basic lead chloride is $\text{PbCl}_2, 7\text{PbO}$, and a basic copper carbonate is $\text{CuCO}_3, \text{Cu(OH)}_2$.

Basic salts are more systematically formulated on the basis of co-ordination number (p. 265). Thus three basic salts of copper are the minerals :



LIME AND THE ALKALIS

Black's researches on the alkalis.—The chemical nature of chalk and lime and of the alkalis was largely explained by the classical researches of Joseph Black (1728-1799).^{*} In his time three alkalis were known, each in two forms, a mild and a caustic (obtained by boiling with lime) :

(1) Mild vegetable alkali (potassium carbonate K_2CO_3) obtained from plant ashes ; caustic vegetable alkali (potassium hydroxide KOH).

(2) Mild marine alkali (sodium carbonate Na_2CO_3) obtained in Normandy and Spain from ashes of plants growing on the sea shore (deep-sea weeds contain the vegetable alkali) ; caustic marine alkali (sodium hydroxide NaOH).

(3) Mild volatile alkali (containing † ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$) obtained by the destructive distillation of bones, from putrefied urine or from the *sal ammoniac* of Egypt ; caustic volatile alkali (ammonium hydroxide NH_4OH , described by Boyle in 1675).

Limestone, chalk and marble are varieties of the same substance, calcium carbonate CaCO_3 , which is neutral and practically insoluble. On strong heating ("burning" ‡) it forms quicklime which is strongly basic and is appreciably soluble in water to form an alkaline solution (lime water).

Before Black's work it was thought that limestone on burning took up a "principle of causticity" from the fire, becoming quicklime, and that this principle was transferred to a mild alkali on boiling with quicklime, thus rendering the alkali caustic.

Black (who worked chiefly with magnesia, the mild form of which is easily decomposed by heat) found that when limestone is heated there is a loss of weight, and a gas which he called "fixed air" (CO_2 , overlooked in the old theory) is evolved. The residue is quicklime :

(1) limestone = quicklime + fixed air.

If the quicklime is slaked and boiled with a solution of mild alkali, the alkali becomes caustic and the quicklime is converted into the original weight of limestone :

(2) quicklime + mild alkali = limestone + caustic alkali.

^{*} Black's paper : "Experiments on Magnesia Alba", etc., published in 1756 as an extension of his dissertation of 1754, may be read in *Alembic Club Reprint* No. 1.

† For a fuller statement of the composition of "sal volatile" see p. 301.

‡ "Burning" is not a very accurate description of the preparation of lime, since combustion of the limestone does not take place, but it is the correct technical name for the process. See p. 50.

If we add equation (1) to equation (2) we find :

(3) mild alkali = caustic alkali + fixed air.

So far from quicklime and caustic alkalis being compounds of limestone and mild alkalis with some caustic principle, they are seen to be simpler than the mild forms and the mild forms part with fixed air in producing the caustic forms. Hence, according to Black, the corrosiveness of quicklime and caustic alkali is an essential property of the pure earth and the pure alkali, respectively, and is not due to any separate principle of causticity.

Black also remarked that :

" when we mix an acid with an alkali [*i.e.* a *mild* alkali], or with an absorbent earth [limestone or chalk], [fixed] air is set at liberty and breaks out with violence ; because the alkaline body attracts it more weakly than it does the acid, and because the acid and air cannot both be joined to the same body at the same time."

When the solution of limestone in acid is mixed with mild alkali the original weight of limestone is precipitated. In this case no fixed air is evolved from the mild alkali although the latter forms a salt with the acid. This is because the fixed air is transferred to the lime with the formation of limestone.

The theory of caustification is thus stated by Black :

" If quicklime be mixed with a dissolved alkali, it likewise shows an attraction for fixed air, superior to that of the alkali. It robs this salt of its air, and thereby becomes mild itself ; while the alkali is consequently rendered more corrosive, or discovers its natural degree of acrimony, or strong attraction for water ; which attraction was less perceivable, as long as it was saturated with air. And the volatile alkali [ammonium carbonate], when deprived of its air, besides this attraction for various bodies, discovers likewise its natural degree of volatility [as ammonia gas], which was formerly somewhat repressed, by the [fixed] air adhering to it, in the same manner as it is repressed by the addition of an acid."

The action of heat on marble.—The evolution of "fixed air" on heating limestone (or marble) may be shown by the following experiment.

Some powdered marble is *strongly* heated in a hard glass tube and a slow stream of heated air is drawn by an aspirator over the marble, then bubbling through lime water in a test-tube (Fig. 33). The lime water becomes milky. This is a characteristic property of carbon dioxide, hence marble on heating decomposes into quicklime and carbon dioxide. (Since the pressure of carbon dioxide over heated marble does not reach atmospheric pressure below a *bright red* heat, it is necessary to sweep away the gas by a current of air ; see p. 50.) The residue in the tube, on cooling, will turn moist red litmus paper blue.

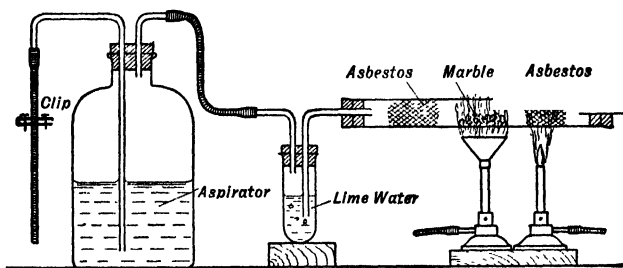


FIG. 33.—Decomposition of marble by heat.

The action of acid on marble.—The weight of carbon dioxide given off from chalk or marble on treatment with acid may be found with the apparatus shown in Fig. 34.

The flask is fitted with a tube tightly packed with cotton wool to keep back spray; the test-tube inside contains 1 gm. of marble and the flask contains 20 c.c. of concentrated hydrochloric acid diluted with its own volume of water. The tube containing the marble is supported by a piece of fine thread passing outside as shown, and the apparatus is weighed.

The rubber stopper is loosened and the tube containing the marble allowed to drop into the acid. The stopper is then quickly and tightly replaced. The marble is allowed to dissolve in the acid.

Since the flask is now filled with carbon dioxide which is heavier than air, this gas must be displaced by aspirating a slow stream of air through the tube fitted with the clip, which was previously kept closed. The clip is again closed and the apparatus weighed. The loss in weight represents the carbon dioxide evolved from the weighed piece (1 gm.) of marble. One gram of marble should give 0.44 gm. of carbon dioxide.

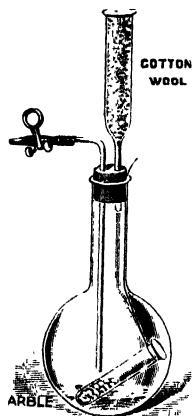


FIG. 34.—Decomposition of marble by acid.

The action of quicklime on mild alkali.—The reaction in the caustification of mild alkali (washing soda) by quicklime is shown in the following experiments.

(1) A piece of pure quicklime (from marble) is weighed and is slaked with water in a porcelain dish. The thin paste is boiled for some time with an excess of washing soda solution. The liquid is diluted with hot distilled water and filtered through a weighed filter paper (the concentrated solution disintegrates filter paper), the precipitate being well washed with hot water. It is then dried and weighed.

The powder on the filter paper is an artificial marble or limestone, which will effervesce with acid. One gram of limestone should be obtained from 0.56 gm. of quicklime, and 1 gm. of marble has been found to contain 0.44 gm. of carbon dioxide. But $0.56 + 0.44 = 1.00$, hence the marble contains only quicklime and carbon dioxide.

(2) An excess of slaked lime is boiled with a solution of washing soda (best in an iron pan). The clear solution when decanted is found to have become caustic (soapy feel; action on red litmus; no or only slight effervescence with acid). On evaporation in a dish a fused mass of caustic soda may be obtained and, as Black found :

"having once evaporated a part of the . . . ley in a bowl of English earthen or stone ware, and melted the caustic with a gentle heat, it corroded and dissolved a part of the bowl, and left the inside of it pitted with small holes." A silver dish should be used, he says, but an iron one, *e.g.* a sand bath, is fairly satisfactory.

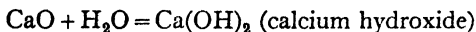
The action of mild alkali on "lime salt".—When a known weight of marble is dissolved in hydrochloric acid, carbon dioxide is evolved with effervescence. The solution formed gives on evaporation a deliquescent salt called calcium chloride, and the same "lime salt" is produced from quicklime and hydrochloric acid but in this case no gas is evolved. By mixing the calcium chloride solution with washing soda, a white precipitate is formed which when filtered, washed and dried, is found to be limestone. The weight of this should equal the weight of marble originally taken. The filtrate from the limestone precipitate when evaporated gives common salt, and this is also produced by the action of hydrochloric acid on either washing soda or caustic soda.

The reactions in Black's experiments can be represented by the following equations :

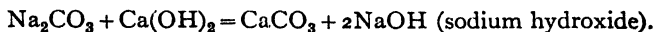
1. Preparation of quicklime (calcium oxide) from limestone (calcium carbonate) :



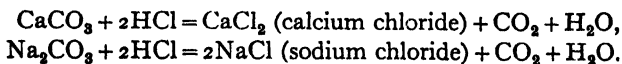
2. Slaking of lime :



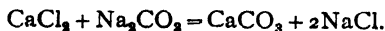
3. Caustification of mild alkali (sodium carbonate) :



4. Action of acid on limestone or mild alkali :



5. Precipitation of lime salt (calcium chloride) by mild alkali :



Limestone.—Calcium carbonate CaCO_3 occurs crystalline as *calcite* (Fig. 35) and in another less common form *aragonite* (Fig. 36). In the massive form calcium carbonate occurs abundantly as *marble*, *limestones* of various kinds, *calc spar* (a very pure transparent variety of which is *Iceland spar*) and *chalk*.

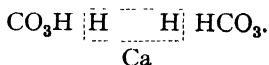


FIG. 35.—Calcite from Guanajuato.
British Museum (Natural History).

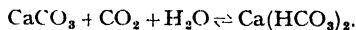


FIG. 36.—Aragonite from Cumberland.
British Museum (Natural History).

Calcium carbonate is only very sparingly soluble in pure water and has a neutral reaction, but it dissolves in water containing carbon dioxide to form an unstable *bicarbonate* $\text{Ca}(\text{HCO}_3)_2$, formed from *two* molecules of the dibasic carbonic acid :



The formula of calcium bicarbonate may be written in the old dualistic notation (p. 42) as $\text{CaO}, 2\text{CO}_2, \text{H}_2\text{O}$. In this soluble form calcium carbonate is transported in nature and is deposited again as carbonate, since the reaction is reversible :



Temporarily hard water contains calcium bicarbonate in solution, formed by the action on calcium carbonate of the carbon dioxide dissolved in the water (see p. 53).

Quicklime.—Calcium carbonate (limestone or marble) when heated to redness decomposes, evolving carbon dioxide and leaving calcium oxide or quicklime CaO . In a closed vessel the decomposition stops at a certain pressure of the carbon dioxide which has a definite value at each temperature ; the system is then in equilibrium :



This pressure is larger the higher the temperature and reaches 760 mm. (when the limestone decomposes freely) at about 900°.

If the carbon dioxide is swept away by a current of air, decomposition is complete. This reaction is applied in making quicklime from limestone or marble ("lime-burning").

In some districts, *e.g.* in High Peak, Derbyshire, the limekiln is filled with blocks of the limestone, and an arch *gh* of lumps of the stone is built over the fire below, the fuel being kept separate from the stone (Fig. 37). The burning goes on for thirty-six to forty-eight hours, the temperature being about 1000°.

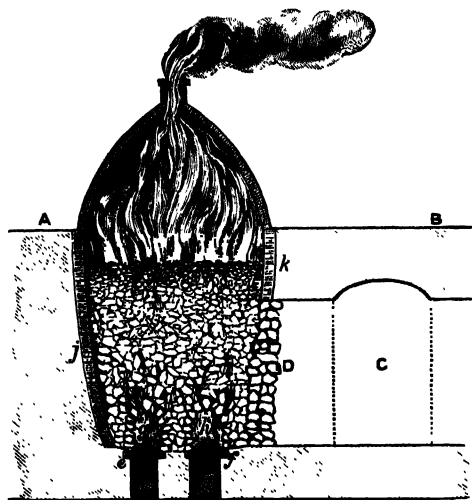


FIG. 37.—Derbyshire limekiln.

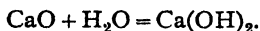
modern limekilns the stone passes down a tall shaft in which it is heated by burning producer gas.

Much of the lime made is used in building as mortar (although this is giving way to cement); it is also used in chemical industries (*e.g.* in making soda and bleaching powder), paper making, tanning, as a fertiliser, etc. Slaked lime is the cheapest base and is used in many technical processes for neutralising acids.

Pure calcium oxide is prepared in the laboratory by heating Iceland spar with the blowpipe in a

crucible with free access of air, until a little of the white opaque residue after cooling and addition of water no longer effervesces with acid. It is a white amorphous mass, which melts and volatilises only at the very high temperature of the electric arc. Lime resists the temperature of the oxyhydrogen blowpipe without more than sintering, and then emits a very bright white light ("limelight"), formerly used for the illumination of optical lanterns.

Slaked lime.—When quicklime is moistened with water it cracks, much heat is evolved and clouds of steam are given off. Finally after addition of sufficient water the lime crumbles down to a fine dry white powder of calcium hydroxide Ca(OH)_2 , known as *slaked lime*, formed by the combination of quicklime and water :



If mixed with an excess of water a paste called *milk of lime* is formed ; if shaken with water slaked lime dissolves sparingly (about $1\frac{1}{4}$ gm. per litre at 15°), producing an alkaline solution called *lime water*. The solubility at 100° is only about half that at room temperature.

Quicklime when exposed to air slowly absorbs moisture and carbon dioxide present in the atmosphere, crumbling to a powder of a mixture of calcium hydroxide and carbonate. Lime water on exposure to air becomes covered with a crust of calcium carbonate.

Lime is used in the preparation of mortar for building purposes. This consists of a thick paste of slaked lime mixed with sand. The hardening of mortar consists in the evaporation of the moisture or its absorption by the bricks, and the slow conversion of the calcium hydroxide into carbonate by atmospheric carbon dioxide. Old mortar effervesces with dilute hydrochloric acid and leaves a residue of sand, but the conversion of the lime into carbonate is very slow. Lime made from limestone containing magnesium carbonate ("magnesian limestone") slakes with difficulty and gives a powdery mixture with water. It is called "poor" lime as distinguished from "fat" lime, which slakes easily and gives a stiff paste with water. No reaction occurs between the lime and sand in mortar.

CHAPTER VI

HARD AND SOFT WATERS

Natural waters.—Natural water contains various impurities present in amounts varying with the source of the water. The following division of natural waters * is convenient: (1) **rain water**, (2) **river water**, (3) **spring**, or **deep well**, water, (4) **sea water**, and (5) **mineral waters**.

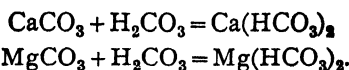
The impurities in natural water are of two kinds: (1) suspended; (2) dissolved, both solids and gases. For chemical purposes water is purified by distillation, preferably in a copper vessel with a copper or pure tin condenser (*cf.* p. 4). When very pure water is required, some potassium permanganate and caustic potash are added to ordinary distilled water and the mixture is distilled until the distillate is free from ammonia when tested with Nessler's solution (p. 363).

Rain water (and hence snow) always contains impurities, especially in towns. Dissolved atmospheric gases (oxygen, nitrogen, carbon dioxide) and common salt (sodium chloride) derived from sea spray carried inland by winds are always present. Nitrous and nitric acids produced by electrical discharges (lightning) are nearly always present as ammonium nitrite and nitrate. In towns the rain contains soot, and sulphuric acid from the sulphur dioxide formed by the combustion of coal, which contains iron pyrites (iron disulphide FeS_2).

River water is rain water which has percolated through the surface soil and contains suspended and dissolved impurities from the soil. Some spring water may be mixed with it. The suspended matter is partly clay and partly organic (vegetable) matter. The dissolved matter consists mainly of salts of calcium and magnesium. The atmospheric carbon dioxide dissolved in the rain, and that taken up from decaying vegetable matter in the soil, forms carbonic acid: $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$. This is a very weak acid, but it dissolves calcium carbonate from limestone or chalk over which the water flows, or that present in the soil, and also

* On water supplies see: W. Garnett, *A Little Book on Water Supply* (Cambridge Press); Rideal, *Water Supplies*; Don and Chisholm, *Modern Methods of Water Purification*; Buswell, *The Chemistry of Water and Sewage Treatment*.

magnesium carbonate, to form soluble calcium and magnesium bicarbonates :



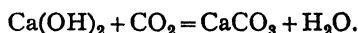
If calcium sulphate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is present in the soil or rocks, this dissolves and sometimes the water may contain calcium chloride CaCl_2 , and magnesium sulphate MgSO_4 and chloride MgCl_2 , from the soil. All these salts produce *hardness* in water.

River water flowing over cultivated land contains in addition to the above impurities sodium chloride and ammonium salts, nitrites and nitrates, formed by bacterial action on the nitrogenous organic matter of vegetable and animal origin.

The purity of the water depends on the nature of the soil. Thames water flowing over soil rich in limestone contains about 157 milligrams of calcium carbonate per litre. Trent water flowing over soil containing gypsum contains 300 milligrams of calcium sulphate per litre. The waters of the Dee and Don draining the Aberdeen granite area contain only traces of dissolved calcium salts, and Glasgow water from Loch Katrine contains only 30 milligrams of total solid matter per litre. Bala Lake water is also very soft.

Spring, or deep well, water differs from river water only in having undergone filtration through porous strata. In this way the suspended matter may be largely removed, leaving the water clear. The organic matter and nitrites, if present, may have been more or less oxidised to nitrates, but the dissolved mineral impurities usually increase.

Temporarily hard water.—The formation of calcium bicarbonate is shown by passing a slow current of washed carbon dioxide into clear lime water (a solution of calcium hydroxide). A white precipitate of calcium carbonate is first produced :



As the carbon dioxide continues to pass this precipitate dissolves and a clear solution of calcium bicarbonate is formed :



The calcium carbonate dissolved as bicarbonate may be precipitated in two ways :

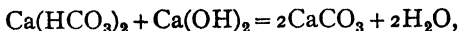
(1) By boiling a portion of the solution in a flask, when carbon dioxide is evolved and a white precipitate of calcium carbonate is formed :



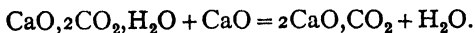
or



(2) By adding to another portion of the solution an equal volume of the lime water, when calcium carbonate is precipitated :



or



Hard water containing calcium bicarbonate therefore deposits a "fur" or "scale" of calcium carbonate (often coloured brown by iron oxide and organic matter) in kettles or boilers, respectively. Such water, which is softened by boiling, is called **temporarily hard water**. It may be softened for use by adding just enough lime (calcium hydroxide) or lime water to precipitate the calcium bicarbonate and then filtering. This is called **Clark's process**.

Waters containing calcium bicarbonate in solution, when they fall in drops from the roofs of caves lose carbon dioxide and deposit calcium carbonate in the form of *stalactites*. The drops falling on the floor of the cave also cause another concretion called a *stalagmite* to grow upwards to meet

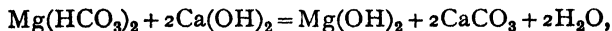


[Photo. Frith & Co. Ltd.]

FIG. 38.—Stalactites and stalagmites in Cox's Cave, Cheddar.

the stalactite (Fig. 38). Small stalactites formed under brickwork arches are derived from the calcium carbonate in the mortar which is dissolved by the carbon dioxide in the rain.

Water containing magnesium bicarbonate $\text{Mg}(\text{HCO}_3)_2$ is not softened by boiling, since magnesium carbonate MgCO_3 is appreciably soluble in water (1 gm. per litre). In this case enough lime must be added in Clark's process to precipitate the sparingly soluble magnesium *hydroxide* :



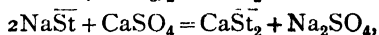
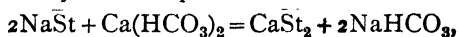
as well as any calcium bicarbonate present.

Ferrous carbonate FeCO_3 , present in some soils, also dissolves in water containing dissolved carbon dioxide, forming ferrous bicarbonate $\text{Fe}(\text{HCO}_3)_2$. On boiling, or exposure to air, a reddish-brown precipitate of ferric hydroxide $\text{Fe}(\text{OH})_3$ ("rust") is thrown down, since the ferrous carbonate is readily oxidised by atmospheric oxygen :



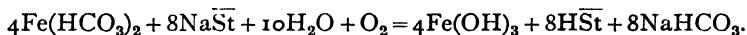
Water containing iron stimulates the growth of a thread-like organism *Crenothrix*, which gives the water a bad taste and causes a precipitate of ferric hydroxide which may stop up pipes. The ferrous bicarbonate may be removed by aeration, when it is precipitated as ferric hydroxide.

All kinds of hard water cause waste of soap, since they react with the soap, which consists of the sodium salts of fatty acids such as stearic acid, and form a slimy precipitate or scum of the calcium and magnesium salts, which also carry some soap down with them :



where $\overline{\text{St}} = \text{C}_{17}\text{H}_{35}\text{COO} -$ is the stearate radical.

If ferrous bicarbonate is present, brown ferric hydroxide is precipitated, causing "iron mould" on fabrics :



Permanently hard water.—Water containing dissolved calcium sulphate is not softened by boiling. The hardness due to calcium sulphate (also to magnesium sulphate and calcium and magnesium chlorides, which are sometimes present) is called *permanent* hardness. The water may in addition possess temporary hardness. If such waters are evaporated in kettles or boilers, calcium sulphate CaSO_4 is deposited as a very hard crystalline "fur" or scale. This is not due to a chemical change, as is the production of calcium carbonate from a temporarily hard water, but to loss of water by evaporation until the saturation point of the dissolved calcium sulphate is reached. (The scale is said to be CaSO_4 not $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.) The solubility also decreases with rise in temperature and at the higher temperatures in steam boilers CaSO_4 is almost insoluble. Such waters cause waste of soap in laundry work for the same reason as temporarily hard water.

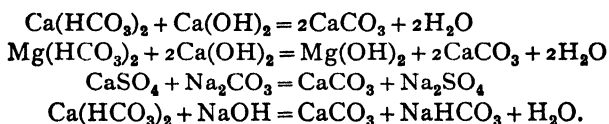
Action of water on lead.—Hardness in drinking water is not known to be injurious to health : the presence of bicarbonates gives the water a refreshing taste and prevents its action on lead pipes.

Very soft water containing dissolved air will dissolve lead and the action is greater in presence of *free* carbonic acid. The dissolved lead is poisonous. Hard water containing dissolved calcium sulphate and

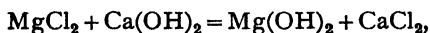
bicarbonate has very little action on lead, as a protective coating is formed on the metal.

This may be shown by placing pieces of clean lead pipe in beakers containing (a) distilled water and (b) tap water. After a few hours the distilled water becomes turbid and gives a black or brown coloration (lead sulphide) with hydrogen sulphide solution. The tap water remains clear and should not give a colour.

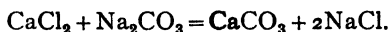
Water softening.—Water for domestic and industrial purposes may require to be softened if it is too hard as it comes from the source. The *temporary hardness* is removed by *Clark's process* (p. 54). For industrial purposes (boilers and laundries) the *temporary* and *permanent hardness* are both removed by adding lime and sodium carbonate; sometimes caustic soda is added :



If magnesium chloride is present, the action of lime is :



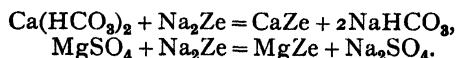
and the calcium chloride must then be precipitated by sodium carbonate :



Calcium carbonate is much less soluble (14 mgm./lit.) than calcium sulphate (gypsum 2 gm./lit. as CaSO_4) and is precipitated. Some calcium carbonate usually remains in the form of a supersaturated solution (p. 6).

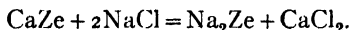
The process of water softening now most widely used is the "base-exchange" or "Permutit" process.* In this the hard water is percolated through granules of a material such as *Permutit*, which is a trade name for an artificial sodium aluminium silicate allied to the natural zeolites. Commercial zeolites are also made from natural greensand (glauconite).

The zeolite may be formulated as Na_2Ze , where Ze stands for the "zeolite radical"; this is often given the composition $\text{Ze} = \text{Al}_2\text{Si}_2\text{O}_7$, or $\text{Al}_2\text{H}_4\text{Si}_2\text{O}_{12}$, but the commercial zeolites contain more silica and approximate to $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, (\text{SiO}_2)_n$, where n varies from 5 to 13. The calcium and magnesium salts in the water react with the zeolite as follows :

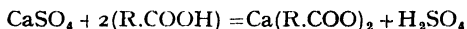


* Plenty of literature on the process is obtainable from water-softening companies.

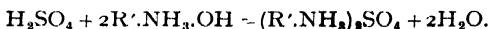
After use the zeolite loses its activity and is then regenerated by percolating with a concentrated solution of common salt, which displaces the calcium and magnesium from the zeolite and replaces these by sodium, so that the mass is ready for use again :



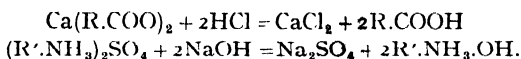
Newer water softeners are synthetic resins containing the groups $-\text{COOH}$ (acidic resins) and $-\text{NH}_2\cdot\text{OH}$ (basic resins). The acidic resins remove basic radicals such as Ca and Mg, forming acids :



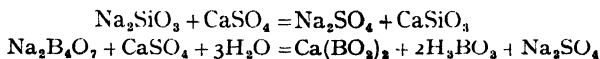
where R is an organic group. The acid formed is then removed by passing the water over the basic resin :



The resins are regenerated by percolating with acid and alkali solutions :



In laundries sodium metasilicate or borax is used in softening water :



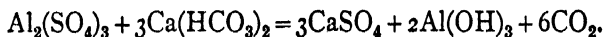
The "hardness" of water is determined by adding from a burette to 100 c.c. of the water a standard soap solution in alcohol, shaking after each addition until a lather is formed which lasts a minute. The soap solution is standardised so that 1 c.c. corresponds with 10 mgm. CaCO_3 , and (after subtracting 1 c.c. for the amount to produce a lather with 100 c.c. of distilled water) the number of c.c. used gives the *degree of hardness* in parts of CaCO_3 (so expressed whether temporary or permanent) per 100,000. Another unit is grains per gallon, and this divided by 0.7 gives parts per 100,000. A soft water has a hardness not exceeding 10° , a medium hard water from 10° to 20° , a hard water from 20° to 30° , and a very hard water above 30° . Thames water has a mean hardness of 20° which is reduced to 5° after lime-softening.

The following analyses of river waters provide material for problems on water softening, the amounts being in parts per 100,000.

	CaCO_3	CaSO_4	MgCO_3	NaCl	SiO_2	Organic matter
Thames - -	14.4	4.5	1.8	2.6	0.8	3.4
Trent - -	0.46	30.1	8.1	2.5	1.0	5.2
Dee (Aberdeen)	1.2	0.17	0.51	1.0	0.2	2.2
Don ,,	3.2	0.2	1.5	1.8	0.75	4.3

Sterilising water.—For use for drinking purposes the water must be filtered and also sterilised if it is likely to contain harmful bacteria. Filtration is carried out through beds of gravel and sand, which become covered with a layer of clay, algae, etc., which removes suspended matter and also many bacteria. If necessary a little aluminium sulphate may

be added to clarify the water from finely suspended clay ; alumina is precipitated and carries down suspended particles and also some bacteria :



The water is sterilised by adding bleaching powder solution, or chlorine gas, or a mixture of chlorine and ammonia (*chloramine process*—which is more effective than chlorine alone) or by bubbling ozonised air through the filtered water, or by exposure to ultraviolet light.

Mineral waters.—Natural waters containing special constituents not present (except in traces) in ordinary water are known as mineral waters. These constituents are : carbon dioxide, ferrous carbonate held in solution by carbon dioxide (*chalybeate waters*), hydrogen sulphide (*hepatic waters*), alkalis, magnesium or sodium sulphates, or iodides.

Sea water contains dissolved salts, especially sodium chloride. An analysis of the water of the Irish Sea, in parts per 1000, is :

NaCl	KCl	MgCl ₂	MgBr ₂	MgSO ₄	CaSO ₄	CaCO ₃	MgI ₂
26·44	0·746	3·151	0·0705	2·066	1·332	0·0475	0·0025

Sea water behaves as a hard water since it contains calcium and magnesium salts and also because the common salt in it precipitates soap as such, or prevents it from forming a solution.

CHAPTER VII

THE PHYSICAL PROPERTIES OF GASES

Boyle's law.—In practice, the volumes of gases, no matter what are the conditions in which they are measured, are always reduced by calculation to the volume the gas would occupy if it were (a) dry, (b) at a temperature of 0°C ., and (c) under a pressure of 760 mm. of mercury. The conditions 0°C . and 760 mm. pressure are called *standard* (or normal) *temperature and pressure*, generally written as S.T.P. (or N.T.P.). The pressure 760 mm. is chosen because it is about the average barometric pressure.

In this calculation we must first know how the volume of a gas varies with the pressure when the temperature is constant. This was found experimentally by Boyle in 1662 and the result is called **Boyle's law** :

The volume of a given mass of gas at constant temperature is inversely proportional to the pressure.

Boyle's law may therefore be stated in the form that, at constant temperature for a given quantity of gas,

$$\text{pressure} \times \text{volume} = \text{constant} ;$$

$$P_1V_1 = P_2V_2.$$

All actual gases deviate somewhat from Boyle's law, which is true only for what is called an *ideal gas*. All common gases except hydrogen are somewhat more compressible than an ideal gas, *i.e.* if the pressure on a volume v is increased from p to np the resulting volume is a little smaller than v/n . The deviation becomes appreciable at high pressures, and many gases are liquefied when the pressure is above a certain value (see p. 116).

Charles's law.—We next require the effect of change of temperature on the volume of a gas at constant pressure. This is given by a law stated by Dalton and by Gay-Lussac in 1801 but often called **Charles's law** (since it was found experimentally by Charles about 1787, but not published). It states that: if the pressure is constant, the volume

of a given mass of gas expands by $\frac{1}{273}$ of its volume at 0°C. for each 1°C. rise in temperature. (*N.B.*—The words “volume at 0°C. ” must never be omitted.)

Let V_0 be the volume at 0°C. The expansion due to a rise in temperature of $t^{\circ}\text{C.}$ will be $\frac{tV_0}{273}$ and the volume at $t^{\circ}\text{C.}$ will be :

$$V_t = V_0 + \frac{tV_0}{273} = V_0 \left(1 + \frac{t}{273} \right) = V_0 \cdot \frac{273+t}{273}.$$

When $t = -273$ the volume is zero, so that if a gas continued to contract at the same rate on cooling to -273°C. it would occupy no volume at that temperature, which is called the **absolute zero**. Actually the gas would become liquid before this temperature was reached, so that this “law”, like Boyle’s law, is only approximately true. If we reckon temperature from -273°C. as zero we obtain the **absolute temperature**, denoted by T . Thus, $0^{\circ}\text{C.} = 273^{\circ}\text{ abs.}$, and $t^{\circ}\text{C.} = (t+273)^{\circ}\text{ abs.}$

If V_1, V_2 are the volumes of a gas at $t_1^{\circ}\text{C.}$ and $t_2^{\circ}\text{C.}$, the equation above shows that :

$$\frac{V_2}{V_1} = \frac{V_0(273+t_2)}{273} \cdot \frac{273}{V_0(273+t_1)} = \frac{t_2+273}{t_1+273} = \frac{T_2}{T_1},$$

that is to say, the volume of a given mass of gas at constant pressure is proportional to the absolute temperature.

We can also transform the equation into :

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}.$$

In most cases it is necessary to correct both for pressure and temperature when these differ from S.T.P. This is done as follows, the separate corrections being first shown.

EXAMPLE 1.*—A gas occupies 224 c.c. under a pressure of 755 mm. What will be its volume under a pressure of 760 mm. if the temperature remains constant?

We use Boyle’s law : *pressure \times volume = constant* ;

$$\therefore 755 \times 224 = 760 \times x,$$

$$\text{or} \quad x = 224 \times \frac{755}{760} = 222.5 \text{ c.c.}$$

It will be noticed that, since the pressure increases, the volume becomes smaller.

* Further examples and explanations of calculations in all parts of this book will be found in Partington and Stratton’s *Intermediate Chemical Calculations* (Macmillan).

EXAMPLE 2.—The volume of a gas at 16° is 450 c.c. What will be the volume at 0° if the pressure remains constant?

We use Charles's law : $\frac{V_1}{T_1} = \frac{V_2}{T_2}$;

$$T_1 = 273 + 16 = 289; V_1 = 450 \text{ c.c.};$$

$$T_2 = 273 + 0 = 273; V_2 = x;$$

$$\therefore \frac{450}{289} = \frac{x}{273}, \text{ or } x = 450 \times \frac{273}{289} = 425.1 \text{ c.c.}$$

EXAMPLE 3.—A volume of gas at 15° and 750 mm. occupies 4.5 litres. Find the volume at S.T.P.

Suppose the pressure changes from 750 mm. to 760 mm. whilst the temperature remains constant at 15° . The volume will become smaller, viz. :

$$4.5 \times \frac{750}{760} \text{ litres.}$$

Now let the pressure remain constant at 760 mm. and change the temperature from 15° to 0° . The volume becomes smaller, viz. :

$$\left(4.5 \times \frac{750}{760}\right) \times \frac{273}{288} = 4.21 \text{ litres.}$$

The general gas law.—For a given mass of gas let V_1 , P_1 , T_1 and V_2 , P_2 , T_2 be the corresponding volumes, pressures and *absolute* temperatures.

Let the gas have initially the pressure, volume and temperature, P_1 , V_1 and T_1 . Let these be changed to the final pressure, volume and temperature, P_2 , V_2 , and T_2 in two steps :

(i) Keeping T_1 constant, let the pressure be changed from P_1 to P_2 . The volume will change to V , which (since the temperature is still T_1 , and not T_2) is not equal to V_2 . The change occurs at constant temperature, so that Boyle's law applies ;

$$\therefore P_1 \times V_1 = P_2 \times V; \therefore V = \frac{P_1 V_1}{P_2}. \dots\dots\dots(i)$$

(ii) Keeping P_2 constant, let the temperature be changed from T_1 to T_2 . Then, since the pressure is P_2 , the volume must become V_2 . Since the pressure is constant, Charles's law applies ;

$$\therefore \frac{V_2}{T_2} = \frac{V}{T_1}. \dots\dots\dots(ii)$$

Substitute V from (i) in (ii) and simplify, then :

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}.$$

This important equation is called the **general gas law**.

Partial pressures.—In a mixture of two (or more) gases the total pressure exerted by the gas is the sum of the partial pressures of the separate gases. The partial pressure is the pressure each gas would exert if it were *separately confined in the whole volume occupied by the mixture*. This result is called Dalton's law of partial pressures, and it is proved by experiment.

The partial pressures can be calculated by Boyle's law when we know the composition of the mixture.

For example, air contains one volume of oxygen to four volumes of nitrogen. Let us suppose that a volume of air is confined in a globe at a pressure of 1 atmosphere. Now suppose the oxygen removed (say by exposing phosphorus to the air in the globe), then the pressure will fall by the amount of the partial pressure of the oxygen. This is the pressure which the oxygen would exert if it alone were present in the globe and Boyle's law shows that this is one-fifth of an atmosphere. The pressure of the nitrogen is similarly four-fifths of an atmosphere. The sum of the partial pressures is 1 atm.

$$= \frac{1}{5} \text{ atm. for the oxygen} + \frac{4}{5} \text{ atm. for the nitrogen.}$$

EXAMPLE.—Let a vessel of 2210 c.c. containing nitrogen at a pressure of 56 cm. of mercury be connected with a vessel of 600 c.c. containing oxygen under 76 cm. pressure and let the gases mix. The temperature is supposed to remain constant.

The total volume is $2210 + 600 = 2810$ c.c.

The partial pressure of the nitrogen in the mixture is the pressure it would exert if this gas alone occupied 2810 c.c.

$$= 56 \times \frac{2210}{2810} = 44.0 \text{ cm.}$$

Similarly, the partial pressure of the oxygen

$$= 76 \times \frac{600}{2810} = 16.2 \text{ cm.}$$

The total pressure of the mixture $= 44.0 + 16.2 = 60.2$ cm.

Correction for moisture in a gas.—In accurate work a correction must be applied to the volume of a gas *measured over water* in order to find the true volume which the gas would occupy if dry.

If water evaporates into a dry gas at constant pressure, the gas will expand. The volume of a given mass of gas is therefore *greater* when it is moist than when it is dry.

Suppose we have a volume of 100 c.c. of moist air, measured over water at 15° , and under a total pressure of 760 mm. This total pressure is the sum of the pressure of the dry air and of the vapour pressure of

water at 15° , viz. 12.7 mm. The pressure of the *dry* air is therefore $760 - 12.7 = 747.3$ mm. If the water vapour were removed by a drying agent from the 100 c.c. of moist air contained in a closed vessel, the pressure would therefore fall to 747.3 mm. If we now increased the pressure of the dry air to 760 mm., the volume would become, by Boyle's law, $100 \times \frac{747.3}{760}$ c.c., and at 0° this would be

$$100 \times \frac{747.3}{760} \times \frac{273}{288} = 93.2 \text{ c.c.}$$

If we had omitted to correct for moisture, the volume at S.T.P. would have been

$$100 \times \frac{273}{288} = 94.8 \text{ c.c.}$$

Drying gases.—Substances such as calcium chloride, quicklime, potassium or sodium hydroxide, concentrated sulphuric acid, and phosphorus pentoxide, which readily take up water vapour, are used in drying gases. In some cases the gas may act chemically on one or other of these, *e.g.* ammonia on sulphuric acid, phosphorus pentoxide and calcium chloride, and the appropriate drying agent must be chosen for each gas. The liquid sulphuric acid may be used in wash-bottles (Fig. 39) and a stream of gas bubbled through it, or it may be absorbed in pumice and the pieces of impregnated pumice packed in a drying tower (Fig. 40), through which the gas is passed. Solid calcium chloride, quicklime and potassium or sodium hydroxide are usually contained in U-tubes (Fig. 27) or drying towers. Phosphorus pentoxide is used dusted over dry glass wool put into a tube. Such apparatus is also used in purifying gases, the appropriate solution or solid being used to absorb the impurity, *e.g.* lead acetate solution to remove hydrogen sulphide from hydrogen.

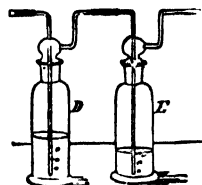


FIG. 39.—Wash-bottles.

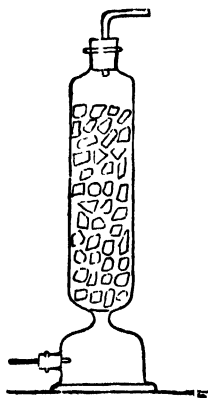


FIG. 40.—Drying tower.

Density of a gas.—The comparative “heaviness” of solids and liquids is measured by the **density**, *i.e.* the weight of unit volume, usually 1 ml. ($= 10^{-3}$ lit.; also called 1 c.c.). Another method is to divide the weight of the solid or liquid by the weight of *an equal volume of water* (taken as a standard liquid), when we obtain the **specific gravity**. Gases are very light so that the weight of 1 ml. would be inconveniently small, and also

they are so very much lighter than water that this would not be a convenient standard of comparison. It is usual, therefore, to take different definitions of density and specific gravity (or **relative density**) in the case of gases or vapours.

(1) The **normal density** or simply **density** of a gas is the weight in grams of 1 litre measured at a temperature of 0° , and under a pressure of 760 mm. of mercury at 0° and sea-level.

(2) The **relative density** (sometimes called **vapour density**) of a gas or vapour is the weight of any volume divided by the weight of *an equal volume of hydrogen* at the same temperature and pressure. Hydrogen is taken as the standard because it is the lightest gas known.

Since equal volumes of all gases expand or contract equally for equal changes of pressure, or temperature, the relative density is the same at all temperatures and pressures.

Determination of gas densities.—The density of a gas is determined by finding (i) the weight W of a vacuous globe (Fig. 41); (ii) the weight W_g of the globe filled with gas at temperature t° and pressure p mm., (iii) the weight W' of the globe filled with water.

The volume of the globe is $(W' - W)$ c.c. and the weight of the gas is $(W_g - W)$ gm. This gas occupies at S.T.P. the volume

$$(W' - W) \times \frac{p}{760} \times \frac{273}{273 + t} = V \text{ c.c.},$$

and the density of the gas is $(W_g - W)/V$ gm. per c.c. The normal density is 1000 times this.

If W_h is the weight of the globe filled with hydrogen, the weight of hydrogen filling the globe is $(W_h - W)$ and the relative density of the gas is

$$\frac{\text{wt. of gas filling globe}}{\text{wt. of hydrogen filling globe}} = \frac{(W_g - W)}{(W_h - W)}.$$

FIG. 41.—Globe for weighing gas.

(No correction for the air displaced by the globe is necessary, provided the atmospheric conditions remain the same, since it is the same in all the weighings and falls out in the subtractions.)

If an air pump is not available, we may find (i) the weight W_a of a thin globe of volume V filled with air, (ii) the weight W_g of the globe filled with gas. The weight of the vacuous globe is W_a minus the weight of air filling the globe, $0.0012V$, where 0.0012 gm. is the weight of 1 c.c. of ordinary air at the average temperature and pressure. The density is

$$[W_g - (W_a - 0.0012V)]/V.$$

The densities of some common gases, in grams per litre at S.T.P., are given below for reference in calculations :

Hydrogen	-	-	0.09	Oxygen	-	-	1.429
Methane	-	-	0.717	Hydrogen sulphide	-	-	1.539
Ammonia	-	-	0.771	Hydrogen chloride	-	-	1.639
Carbon monoxide	-	-	1.250	Argon	-	-	1.784
Nitrogen	-	-	1.251	Carbon dioxide	-	-	1.977
Ethylene	-	-	1.260	Nitrous oxide	-	-	1.978
Air (dry, CO ₂ free)	-	-	1.293	Sulphur dioxide	-	-	2.927
Nitric oxide	-	-	1.340	Chlorine	-	-	3.214

The true weight in vacuum of a globe filled with gas is the apparent weight in air *plus* the weight of air displaced, $W_0 + 0.0012V$. The latter depends on the temperature, pressure, and moistness of the air, which may vary during weighings. The surface of the globe also carries a film of moisture which varies with the moistness of the air. To eliminate these errors Regnault in 1845 made use of a *compensating globe* of as nearly as possible identical weight and volume as the gas globe, and hung on the other arm of the balance. Both globes are then equally affected and corrections are eliminated. A correction still necessary was pointed out by Lord Rayleigh in 1882, viz. the *shrinkage* of the gas globe on exhaustion. This results in the globe displacing rather less air when vacuous than when full of gas. The shrinkage is found by pumping out the globe in a closed tank of water and observing the fall in level of water in a narrow tube attached to the tank. With a globe of 2 litres the shrinkage correction is 0.6 mgm. on the weight of hydrogen filling the globe, and this raises Regnault's value of 0.08968 for the normal density of hydrogen to 0.08988.

The methods for finding the densities of vapours are described in Chapter IX.

Diffusion of gases.—Hydrogen contained in an open *inverted* jar rapidly diffuses out and air enters ; this movement takes place in opposition to gravity since hydrogen, the lighter gas, moves downwards and air, the heavier gas, moves upwards. Döbereiner in 1823 found that hydrogen confined over water in a cracked flask escaped into the surrounding air, the water rising in the neck of the flask. Graham showed in 1831 that as the hydrogen escapes air enters the flask, and since the pressure inside is reduced hydrogen must diffuse out more rapidly than air diffuses in. If the flask is covered with a bell-jar of hydrogen no change in the level of water occurs.

The diffusion of gases may be illustrated by the apparatus shown in Fig. 42. A porous clay pot such as is used in batteries is fitted by a rubber bung to a tube passing into a Woulfe's bottle containing coloured water. Dipping into the coloured water is a glass tube drawn out to a jet above.

A large beaker of hydrogen is inverted over the pot, when hydrogen diffuses into the latter more rapidly than air passes out and the increase of pressure causes the water to issue from the jet in the form of a fountain.

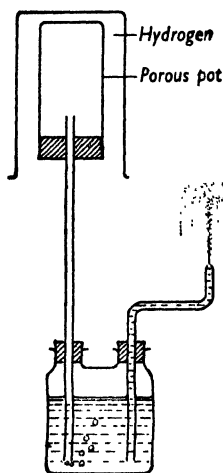


FIG. 42.—Diffusion of hydrogen through a porous pot.

If the beaker is removed, hydrogen inside the pot diffuses out into the air more rapidly than air enters, so that the pressure is reduced. Coloured water thus rises in the vertical tube attached to the pot.

Graham's law.—Graham's apparatus for measuring the rates of diffusion of gases consists of a glass tube closed at one end with a thin plug of plaster of Paris. This tube is filled with hydrogen over mercury (Fig. 43). The mercury rises in the tube and the latter is sunk so as to keep the levels constant. After a certain time all the hydrogen diffuses out and the tube contains only air which has diffused in. The volume of this air is the volume diffusing in the same time as the whole of the hydrogen originally contained in the tube. The inverse ratio of these *volumes* gives the ratio of the *times* required for the diffusion of equal volumes. In

this way Graham in 1833 found the following law of diffusion :

The rate of diffusion of a gas is inversely proportional to the square root of its density.

EXAMPLE 1.—100 c.c. of hydrogen are confined in a diffusion tube exposed to air. When change of volume ceases, what volume of air will have entered the tube?

The volumes diffusing are in the inverse ratio of the square roots of the densities ;

$$\therefore \frac{\text{volume of hydrogen}}{\text{volume of air}} = \frac{\sqrt{1.293}}{\sqrt{0.09}};$$

$$\therefore \text{vol. of air} = 100 \times \frac{\sqrt{0.09}}{\sqrt{1.293}} = 26.4 \text{ c.c.}$$

EXAMPLE 2.—16.8 c.c. of chlorine diffused in the same time as 100 c.c. of hydrogen. Find the relative density of chlorine.

Let x = relative density of chlorine. The volumes diffusing in equal times are in the inverse ratio of the square roots of the densities. Since the relative density of hydrogen is 1,

$$\therefore \frac{100}{16.8} = \frac{\sqrt{x}}{\sqrt{1}} = \sqrt{x};$$

$$\therefore x = 35.4.$$

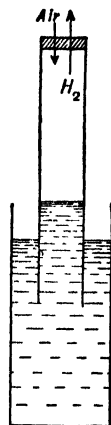


FIG. 43.—Graham's apparatus.

Effusion.—In effusion (also studied by Graham) a gas is forced by pressure through a small hole in a metal plate exposed to the air. The relative rates of effusion of different gases are in the inverse ratio of the square roots of the densities. By means of this law the molecular weights of different gases may be compared. The apparatus used is Bunsen's effusimeter.

A glass cylinder with marks at m_1 , m_2 is placed in a cylinder of water (Fig. 44). At the top of the tube is a stopcock communicating with the free air through a tube closed by a thin platinum plate, in which a hole has been pierced with a fine needle. The tube is filled with gas to a level below m_1 and the tap is opened. The gas streams out through the fine hole and the time required for the liquid surface to pass from m_1 to m_2 is taken by a stop-watch. The experiment is repeated with a gas of known molecular weight, *e.g.* oxygen. If mercury is used, a float is fitted inside the tube, having a line marked on its upper end. The time taken for this mark to pass between two marks on the upper surface of the cylinder is noted.



FIG. 44.—Bunsen's effusimeter (Ostwald).

If t_1 , t_2 are the times of effusion of equal volumes of two gases of densities D_1 , D_2 in the same apparatus, then :

$$\frac{t_1}{t_2} = \frac{\sqrt{D_1}}{\sqrt{D_2}}.$$

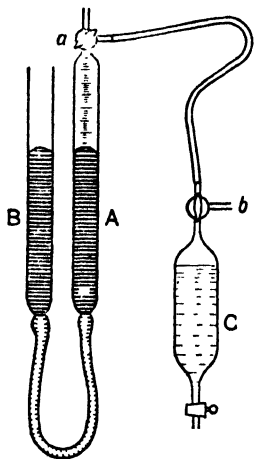


FIG. 45.—Absorptiometer.

Solubility of gases.—The experiment described on p. 5 shows that water can dissolve air. The solubility of a gas in a liquid may be measured by the apparatus shown in Fig. 45, called an absorptiometer.

The gas is measured over mercury in the burette *A* and the volume reduced to S.T.P. Part of the gas is then passed into the absorption vessel *C*, the volume of liquid, *e.g.* water previously boiled to expel dissolved air, remaining in contact with the gas being the original volume minus the volume run out. *A* and *C* are connected by a flexible lead tube. The gas is shaken with the liquid until the solution is saturated. The pressure is adjusted by the levelling tube *B*. The contraction in

volume is then read off on the burette and corrected for the vapour pressure of the liquid, temperature and barometric pressure. In accurate experiments the vessel C must be immersed in a bath of water at constant temperature. If the gas is very soluble (*e.g.* ammonia, hydrochloric acid) it is passed into a measured volume of water until the latter is saturated. The amount of gas dissolved is then found by chemical analysis. The volume of gas reduced to S.T.P. which saturates 1 volume of water (or other liquid) is called the **absorption coefficient**.

From experiments it is found that the amount of gas dissolved by a fixed volume of liquid depends upon: (1) the chemical composition of the gas and of the liquid, (2) the temperature, (3) the pressure. The effect of pressure is given by **Henry's law** (1803):

The weight of gas absorbed by a fixed volume of a liquid at a constant temperature is proportional to the pressure

Since the volume of a given weight of gas at a fixed temperature is inversely proportional to the pressure, *a given volume of liquid absorbs the same volume of gas at all pressures.*

Henry's law does not apply to very soluble gases, such as ammonia at the ordinary temperature or hydrogen chloride in water. It does not hold *accurately* for carbon dioxide. At 100° the solubility of ammonia follows the law.

If the partial pressure of a gas above its solution can be reduced to zero, all the dissolved gas will be expelled. This can usually be effected: (1) by reducing the pressure above the solution by an air-pump; (2) by passing a stream of indifferent gas through the solution (*e.g.* nitrogen through aqueous ammonia); or (3) by boiling the solution, when the dissolved gas is driven off with the steam.

In some cases it is impossible to remove all the gas by boiling, etc., as when the gas and solvent evaporate *together* to form a vapour of the same composition as the solution, the latter then evaporates as a whole. This happens with a solution of hydrochloric acid (see p. 158). The solution then distils at a constant temperature like a pure substance, but the constant composition of the distillate and residue varies with the total pressure under which the liquid is distilled whilst the composition of a pure substance is constant (Roscoe and Dittmar, 1860):

cm. Hg	5	76	100	180	250
per cent. HCl	23.2	20.24	19.7	18.7	18.0

Solubility of a mixture of gases.—*The amount of any one gas dissolved from a mixture of gases is proportional to its partial pressure, when the gas has come into equilibrium with the liquid.* This is **Dalton's extension of Henry's law.**

The absorption coefficients of nitrogen, oxygen and argon in water at 0°, and the percentages by volume of these gases in dry air free from carbon

dioxide, are given below. The partial pressures are proportional to the volume percentages :

<i>Gas</i>	<i>Percentage by vol.</i>	<i>Partial pressure (total = 1 atm.)</i>	<i>Absorption coefficient</i>
Nitrogen - -	78	0.78	0.0239
Oxygen - -	21	0.21	0.0489
Argon - -	1	0.01	0.053

By multiplying the partial pressures by the absorption coefficients, the volumes of the three gases dissolved in 1 vol. of water saturated with a large volume of air (constant composition) are found to be :

nitrogen, 0.01864; oxygen, 0.01027; argon, 0.00053; sum, 0.02944.

When the dissolved gas is expelled by boiling it will have this composition, or, expressed in percentages by volume, it will contain :

nitrogen, $\frac{1.864}{0.02944} = 63.3$; oxygen, $\frac{1.027}{0.02944} = 34.9$; argon, $\frac{0.053}{0.02944} = 1.8$.

The proportions of oxygen and argon have increased, since these gases are more soluble than nitrogen in water. By shaking water with an excess of this gas, and expelling the dissolved part, the latter will be still further enriched in oxygen, and so on. After eight repetitions the gas will contain over 90 per cent. of oxygen.

Partition coefficient.—If a liquid or solid substance *C* is soluble in each of two non-miscible solvents *A* and *B*, and is shaken with both solvents (or a solution of the substance in one solvent is shaken with the other solvent) until equilibrium is reached, the substance *C* is shared by the two solvents. This partition of *C* occurs in such a way that the ratio of its concentrations in the two solvents is a constant for a particular temperature (Berthelot and Jungfleisch, 1872). This constant is called the **partition** (or **distribution**) **coefficient** (or **ratio**).

Let C_A be the concentration of the substance *C* in the solvent *A*, in gm. per c.c., and C_B its concentration in the solvent *B*. Then if *k* is the partition coefficient :

$$\frac{C_A}{C_B} = k.$$

If the same unit of concentration is used for both solutions the partition coefficient is independent of this unit. The partition coefficient depends on the chemical compositions of the dissolved substance and the two solvents and on the temperature.

EXAMPLE.—10 c.c. of carbon disulphide and 10 c.c. of water were shaken with iodine at 18°. The iodine was found to be present in the following amounts :

1.74 gm. iodine in 10 c.c. of carbon disulphide;
0.0041 gm. iodine in 10 c.c. of water.

The partition coefficient of iodine between carbon disulphide and water is equal to the ratio :

$$k = \frac{\text{conc. in carbon disulphide}}{\text{conc. in water}} = \frac{1.74}{10} \bigg/ \frac{0.0041}{10} = 424.$$

In 1891 Nernst pointed out that the ratio $k = C_A/C_B$ is constant only when the solute C has the same molecular weight in each of the two solvents A and B . If the value of k is not constant the molecular weight of the substance is different in the two solvents.

The following figures give the concentrations in grams per 100 c.c. of benzoic acid distributed between benzene and water :

c_1 = concentration in aqueous layer	-	0.15	0.195	0.289
c_2 = " " benzene "	-	2.42	4.12	9.7
c_1/c_2	-	-	0.062	0.047
$c_1/\sqrt{c_2}$	-	-	0.0964	0.0961
				0.0928

The values of c_1/c_2 are not constant and hence it may be assumed that the molecular weights of benzoic acid in water and benzene are different. If it is assumed that the acid exists in benzene mostly as double molecules, $(C_6H_5CO_2H)_2$, or a *dimeric form*, the law of mass action (see Chap. XIX) requires that: $c_1/\sqrt{c_2} = \text{const.}$, since the concentration of single molecules in benzene is proportional to $\sqrt{c_2}$. This result, it will be seen, is approximately obtained.

CHAPTER VIII

THE LAWS OF CHEMICAL COMBINATION AND THE ATOMIC THEORY

It has been emphasised that progress was made in Chemistry only when chemical changes were studied *quantitatively*, and as a result of such experiments certain general laws were discovered. These are :

- (1) The Law of Conservation of Mass (or of Indestructibility of Matter).
- (2) The Law of Constant Proportions.
- (3) The Law of Multiple Proportions.
- (4) The Law of Reciprocal Proportions, or the Law of Equivalent Proportions.
- (5) The Law of Gaseous Volumes.

The first two have been discussed in Chapter II, and the Law of Gaseous Volumes will be studied in Chapter IX. The remaining laws will now be considered. The *explanation* of these laws is given by the Atomic and Molecular Theories, but the laws themselves are purely experimental and independent of theory.

The law of multiple proportions.—As a result of some theoretical reasoning about gases, John Dalton about 1803 concluded that :

If two elements form more than one compound, the weights of one element which combine with identical weights of the other are in the ratio of whole numbers, usually small.

This Law of Multiple Proportions was proved experimentally by Dalton in the cases of compounds of oxygen with nitrogen and carbon, and compounds of hydrogen with carbon. A striking example is supplied by the five oxides of nitrogen, which have the following percentage compositions by weight :

	<i>Nitrous oxide</i>	<i>Nitric oxide</i>	<i>Nitrogen trioxide</i>	<i>Nitrogen tetraoxide</i>	<i>Nitrogen pentoxide</i>
Nitrogen -	63.7	46.7	36.9	30.5	25.9
Oxygen -	36.3	53.3	63.1	69.5	74.1

The weights of oxygen combined with 100 parts of nitrogen are 57, 114, 171, 228 and 285. If each number is divided by the smallest, 57, we obtain the simple whole numbers 1, 2, 3, 4 and 5, which agree with the Law of Multiple Proportions.

Dalton's theory was not published until 1807 and in 1808 Wollaston found an example of the law in potassium carbonate and potassium bicarbonate. When 0.1 gm. of the bicarbonate reacts with hydrochloric acid in a tube filled with and inverted over mercury, it evolves the same volume of carbon dioxide as the potassium carbonate obtained by heating 0.2 gm. of bicarbonate in a crucible. Hence the bicarbonate on heating loses exactly half its carbon dioxide. Thomson in 1808 showed that potash reacts with oxalic acid to form two salts, and the acid oxalate requires for its formation exactly twice as much acid as the normal salt. Wollaston discovered a third oxalate which requires, for identical weights of potash, exactly twice as much oxalic acid as the acid oxalate.

The law of multiple proportions thus applies to the reactions of compounds (*e.g.* acids and bases) as well as elements.

The law of equivalent proportions.—It is found that 23 gm. of sodium combine with 1 gm.* of hydrogen to form sodium hydride and with 35.5 gm. of chlorine to form sodium chloride, and the *equivalent weights* of sodium and chlorine with respect to combination with hydrogen are 23 and 35.5. Also, 23 parts of sodium combine with 35.5 of chlorine to form sodium chloride. Thus, the weights of sodium and chlorine which separately combine with 1 part by weight of hydrogen are also the weights in which sodium and chlorine combine with each other.

If 23 gm. of sodium are heated in hydrogen chloride gas, 1 gm. of hydrogen is displaced whilst at the same time 35.5 gm. of chlorine combine with 23 gm. of sodium. Hence 23 parts of sodium can combine with 1 part of hydrogen and also displace it from its compound with another element.

The generalisation of this result was discovered by Richter in 1792 and is called the **Law of Reciprocal Proportions**, or the **Law of Equivalent Proportions**, or the **Law of Combining Weights** :

The weights of two or more elements A and B which combine separately with identical weights of another element C, are either the weights in which A and B combine together or are related to them in the ratio of whole numbers, usually small.

This is illustrated by the following experimental results :

<i>1 part of hydrogen combines with :</i>	<i>1 part of hydrogen is displaced by :</i>	<i>8 parts of oxygen combine with :</i>
8 or 16 of oxygen	9 of aluminium	35.5 of chlorine
35.5 of chlorine	12 of magnesium	12 of magnesium
80 of bromine	20 of calcium	20 of calcium
127 of iodine	23 of sodium	23 of sodium
16 of sulphur	28 of iron	18.66 or 28 of iron
20 of calcium	32.5 of zinc	31.5 or 63 of copper
23 of sodium	59.5 of tin	29.75 or 59.5 of tin
63 of copper	63 of copper	100 or 200 of mercury

* More accurately 1.008 gm.; see p. 73.

35.5 parts of chlorine
combine with :

12 of magnesium
20 of calcium
23 of sodium
32.5 of zinc
18.66 or 28 of iron
29.75 or 59.5 of tin
31.5 or 63 of copper
100 or 200 of mercury

Weights of metals displacing
one another from compounds :

12 of magnesium
20 of calcium
28 of iron
31.5 of copper
32.5 of zinc
59.5 of tin
100 or 200 of mercury
107.9 of silver

The figures in this table agree with the Law of Equivalent Proportions and show the weights of various elements which combine together or displace one another from compounds. These are called **combining weights** or **equivalent weights** or (usually) **equivalents**. In some cases an element has more than one equivalent but these are always in a whole number ratio ; in the cases of oxygen, copper, tin and mercury this is 1 : 2 ; in the case of iron it is 2 : 3.

In forming such a table of equivalents, the equivalent of a standard element must be chosen ; Dalton took hydrogen as 1 (since its equivalent is the smallest of all) ; Berzelius took oxygen = 100. When hydrogen = 1, the equivalent of oxygen is not quite 8 (see p. 136) ; at present the standard is oxygen = 8, when the accurate value for hydrogen is 1.008.

Normal solutions.—Since compounds, *e.g.* acids and alkalis, react in definite proportions it is possible to determine the equivalent weights of compounds as well as elements, and the law of equivalents was actually discovered with compounds.

Cavendish in 1766 and 1788 showed that the ratio of the quantities of two acids which neutralise identical weights of one alkali was also the ratio of the quantities of the acids which neutralise identical weights of another alkali or of marble, and he called these weights *equivalents*. Richter in 1792 found that when solutions of neutral salts are mixed the solution remains neutral, showing that when the acid of one salt reacts with the base of the other and *vice versa* no free acid or base is left over. Hence the weights of acid and base in both salts are equivalents.

In order to find when the acidic or alkaline properties disappear we make use of **indicators**, which are dyes having different colours in acid and alkaline solutions.

Indicator	Colour in acid solution	Colour in alkaline solution
Litmus -	Red	Blue
Methyl orange -	Pink	Yellow
Phenolphthalein -	Colourless	Crimson

The acid is added from a burette to a measured volume of an alkali solution with an indicator and the process is called **titration**.

A normal (*N* or *N*) solution is one containing the equivalent weight of active substance in 1 litre of solution. A decinormal (*N*/10 or 0.1 *N*) solution contains one-tenth of an equivalent per litre, and so on. Normal solutions of all acids contain 1.008 gm. of acidic hydrogen per litre; normal solutions of oxidising agents contain the equivalent of 8 gm. of active oxygen per litre.*

Determination of equivalents.—Equivalents are determined experimentally in several ways,† some of which will have been studied in the elementary laboratory :

(1) The weight of an element combining with or (more commonly) displacing 1.008 gm. of hydrogen is found. This can be done with metals which dissolve in acids or alkalis with evolution of hydrogen, the volume of which is measured.

(2) The weight of a metal displaced from a solution of one of its salts by the equivalent of another metal in class (1) is found. Thus, the equivalent of zinc is first found by measuring the hydrogen evolved by zinc from an acid, and the weights of copper and lead precipitated by a known weight of zinc from solutions of copper sulphate and lead acetate are then determined. (Magnesium displaces copper very incompletely from copper sulphate solution.)

(3) The weight of an element combining with 8 parts of oxygen is found either directly, as when magnesium or tin is heated in air or oxygen, or indirectly when a metal such as tin reacts with nitric acid and the product is heated (p. 19); or an oxide such as mercuric oxide is decomposed by heat, or one such as copper oxide is reduced by heating in hydrogen (pp. 15, 136). Potassium chlorate may be decomposed by heating and the oxygen evolved measured, when the equivalent of potassium chloride may be calculated.

(4) The weight of a metal combining with 35.5 parts of chlorine is found. Silver may be heated in a stream of chlorine, or a known weight of silver dissolved in nitric acid and the silver nitrate precipitated as chloride, which is weighed. The weight of silver (after dissolving in nitric acid) required to precipitate a known weight of potassium chloride or other soluble chloride will give the equivalent of the latter. Since 107.9 gm. of silver combine with 35.5 gm. of chlorine the equivalent of silver is 107.9 and this weight reacts with an equivalent of a chloride.

(5) A known weight of one compound is converted into another compound. If the equivalent of the first compound is known that of the second, and hence the equivalent of an element in it, can be calculated. Potassium chloride is converted into potassium nitrate by repeated

* See Partington and Stratton, *Intermediate Chemical Calculations*, Chapter VI.

† For further details see Partington and Stratton, *Intermediate Chemical Calculations*, Chapter IV.

evaporation with concentrated nitric acid. If the equivalent of potassium chloride is known (from experiments described above) that of potassium nitrate is found. If the equivalent of potassium is known that of nitrogen can be calculated.

An apparatus for the determination of the equivalent of a metal by method (1) is shown in Fig. 46. A suitable weight of the metal is put into the small tube which is supported in the flask containing the acid or alkali solution by a thread pinched by the rubber stopper. The apparatus is fitted together, the bottle being filled with water. The metal is brought into the liquid by loosening the stopper for a moment, when hydrogen is evolved and displaces water from the bottle into the measuring cylinder when the clip is opened. When action ceases and the flask has cooled to room temperature, the volume of water in the cylinder is read off after equalising the levels. The gas volume is reduced to c.c. at S.T.P. and when multiplied by 0.00009 gives the weight of hydrogen displaced by the weight of metal taken. The weight of metal displacing 1.008 gm. of hydrogen is the equivalent. Zinc, magnesium, iron and calcium may be dissolved in cold dilute hydrochloric acid, tin in hot concentrated hydrochloric acid, and aluminium in a mixture of equal volumes of concentrated hydrochloric acid and water or in warm dilute sodium hydroxide solution.

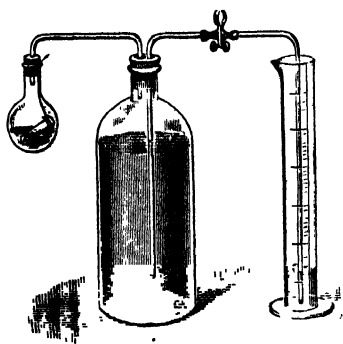


FIG. 46.—Apparatus for determination of equivalents.

Exact determination of equivalents.—The equivalents of some important elements were accurately determined by the Belgian chemist Jean Servais Stas (1813-1891), whose numbers were accepted for a long time as the best values.*

Stas began with an analysis of potassium chlorate, which on heating gives off oxygen and leaves potassium chloride. He found that 127.2125 gm. of potassium chlorate gave on heating 77.4023 gm. of potassium chloride, hence the oxygen given off weighed 49.8102 gm. Potassium chlorate is known to contain 6 equivalents of oxygen, hence the equivalent of potassium chloride, x , is given by :

$$6 \times 8 : x = 49.8102 : 77.4023 ; \therefore x = 74.59.$$

14.427 gm. of potassium chloride gave on precipitation with silver nitrate solution 27.732 gm. of silver chloride, hence the equivalent of silver chloride is given by

$$74.59 : x = 14.427 : 27.732 ; \therefore x = 143.37.$$

101.519 gm. of pure silver when heated in a current of chlorine gave 134.861 gm. of silver chloride, so that the equivalent of silver is given by

$$143.37 : x = 134.861 : 101.519 ; \therefore x = 107.93.$$

Hence the equivalent of chlorine is $143.37 - 107.93 = 35.44$, and the equivalent of potassium is $74.59 - 35.44 = 39.15$.

In 1895 Morley determined the combining ratio of hydrogen and oxygen with great care (p. 138) and found 1 : 7.9395 ; Scott (1893) (p. 139) and Burt and Edgar (1916) in accurate researches found 1 : 7.938. The equivalent of chlorine was determined with reference to hydrogen by Dixon and Edgar (1905) and Edgar (1908) by burning hydrogen and chlorine together, and by Gray and Burt (1909) from the density of hydrogen chloride gas, and the decomposition of the latter by heated aluminium with liberation of hydrogen. The equivalent of chlorine so found, 35.187 (H = 1) referred to oxygen = 8.000, is thus

$$35.187 \times 8.000 \div 7.938 = 35.458,$$

which differs from Stas's figure by as much as 1 in 1500.

The modern equivalents of most of the important elements are based on the equivalents of silver, chlorine or bromine. Oxygen appears in few direct ratios and practically no oxides are suitable for exact analysis. The oxides of metals cannot usually be obtained sufficiently pure.* Of the fundamental secondary standards, bromine forms a most unstable oxide, the oxides of chlorine are explosive and difficult to prepare in a state of purity, and pure silver oxide cannot be obtained. On the oxygen standard the value for nitrogen was until very recently involved as an intermediate link in the ratio *silver/silver nitrate*.

T. W. Richards prepared silver nitrate from pure silver and found that if the combining weight of nitrogen is 14.008, as the physical method of gas densities indicates, then that of silver must be 107.88. He was at first not inclined to alter Stas's figure, 107.93, but since the rejection of the newer figure for nitrogen was clearly impossible in the face of several confirmatory researches, Richards fixed silver arbitrarily as 107.880, and took this as the basis of his figures.

Richards found that Stas's silver, distilled in a lime retort with the oxyhydrogen blowpipe, contained a little oxygen. Richards prepared his silver by reducing recrystallised silver nitrate and fused it in hydrogen.

* It is commonly stated that "hydrogen combines with only a few elements" and that "oxygen compounds are more suitable for analysis than hydrogen compounds". Neither of these statements is correct in the light of modern knowledge, and examination candidates are advised not to repeat them.

Moles and Clavera (1927), by a very accurate determination of the limiting density (p. 83) of nitrogen, found the combining weight 14.0082 ± 0.00004 , which requires silver to be 107.880. Hönigschmid and Sachleben (1929) by heating barium perchlorate in hydrogen chloride gas to give barium chloride and then precipitating silver chloride from this by a silver salt, were able to calculate a ratio *silver/oxygen* which gave 107.880 for the combining weight of silver.

The existence of three isotopes (16, 17 and 18) in ordinary oxygen makes the "chemical" atomic weights, determined with respect to $O=16.000$, really about 2 parts in 10,000 smaller than those determined (say by the mass spectrograph) by "physical" methods, which are referred to the isotope $^{16}O=16.000$ (Aston, *J. Chem. Soc.*, 1932, p. 2890).

THE ATOMIC THEORY

The atomic theory.—The law of conservation of mass, the law of constant proportions, the law of multiple proportions and the law of equivalent weights were first explained on the basis of the atomic theory by John Dalton in 1803.* The atomic theory (see p. 21) supposes matter to be composed of very small indivisible particles called atoms, from the Greek meaning "something which cannot be cut". Leukippos and Demokritos, the Greek philosophers, about 450 B.C. made use of the atomic theory in a rudimentary and qualitative form.

Dalton's atomic theory asserts that :

(1) The chemical elements are composed of very minute particles of matter called atoms, which remain undivided in all chemical changes.

The atom is the smallest particle of an element which can take part in a chemical change.

(2) Each kind of atom has a definite *weight*. Different elements have atoms differing in weight.

(3) Atoms combine in simple numerical ratios, *e.g.* 1 atom *A* + 1 atom *B*; 1 atom *A* + 2 atoms *B*; 2 atoms *A* + 1 atom *B*; 2 atoms *A* + 3 atoms *B*, etc.

These simple assumptions will explain the laws of chemical combination.

In the first place, atoms are indestructible in chemical changes, so that we see the necessity of the *law of conservation of mass*. Second, the molecules of a compound are all alike, formed of fixed numbers of atoms

* See *Alembic Club Reprint No. 2*. The story that Dalton was led to the atomic theory from results of his analyses of methane and ethylene, giving a multiple ratio of 1 : 2 for carbon combined with identical weights of hydrogen, has long been known to be incorrect. The true origin of the theory is sketched in Partington's *A Short History of Chemistry*, p. 174.

of its elements. This explains the *law of constant proportions*. Third, if elements combine in more than one proportion, the examples under (3) explain the *law of multiple proportions*. Last, if we consider the compounds of one element *A* with two other elements *B* and *C*, some whole numbers of atoms of *B* or of *C* will be combined with a certain number



FIG. 47.—JOHN DALTON (1766-1844).

of atoms of *A* in each case. Now when *B* and *C* combine to form a compound, they will also do so in whole numbers of atoms. Hence the weights of *B* and *C* which combine together are either the same as the weights of *B* and *C* which *separately* combine with a fixed weight of *A*, or are simple multiples of them. This is the *law of equivalent proportions*.

Atomic weights.—The absolute weights of atoms are very small and Dalton attempted to find only the relative weights, taking the weight of the lightest atom, that of hydrogen, as unity. The atomic weight of an element is then the number giving the ratio of the weight of an atom of that element to the weight of an atom of hydrogen.

It has been explained (p. 73) that the equivalent of hydrogen, which is the same as its atomic weight, is now taken as 1.008. Since the atomic weight of oxygen is twice the equivalent, viz. 16, the atomic weight of a given element is either 1.008 times the ratio of the weight of an atom of the element to the weight of an atom of hydrogen, or 16 times the ratio of the weight of the atom to the weight of an atom of oxygen. In both cases the standard element is a mixture of isotopes (see p. 259).

The equivalent of an element will, by definition, be either the atomic weight itself or related to it in a simple manner, *i.e.* a simple fraction of it, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{2}{3}$, $\frac{2}{5}$, etc., since 1 atom of the element combines with 1, 2, 3, etc., atoms of hydrogen, or two atoms of the element with 3, 5, etc., atoms of hydrogen, and so on.

The ratio of the atomic weight to the equivalent is equal to the **valency** of the element :

$$\text{Valency} = \frac{\text{Atomic Weight}}{\text{Equivalent}}.$$

The valency of oxygen is $16/8 = 2$; that of copper is $63/31.5 = 2$ in the *cupric* compounds and $63/63 = 1$ in the *cuprous* compounds.

If the absolute weight of *one* atom can be found those of all the others are found by multiplication of this by the ratios of the atomic weights. In recent years (p. 101) the weight of the hydrogen atom has been found to be 1.66×10^{-24} gm.

Dalton's original atomic theory provided no means of determining even the relative weights of atoms. Although 8 parts of oxygen combine with 1 part of hydrogen, we do not know how many atoms of each element the molecule of water contains. If it contains 1 atom of each element (as Dalton supposed), the atomic weight of oxygen is 8, but if it contains 2 atoms of hydrogen to 1 atom of oxygen, as the volume ratio of the combining gases would suggest, the atomic weight of oxygen is $2 \times 8 = 16$.

The method of finding the formulae of gaseous compounds, and hence the relative weights of atoms, was first explained by Avogadro in 1811 (see Chapter IX).

CHAPTER IX

THE DETERMINATION OF ATOMIC AND MOLECULAR WEIGHTS

Gay-Lussac's law of gaseous volumes.—The relative combining volumes of hydrogen and oxygen were found by Cavendish in 1784 (p. 35) to be very nearly 2 to 1. Humboldt and Gay-Lussac in 1805 confirmed this result and Gay-Lussac, impressed by the simplicity of the ratio, extended the researches to other chemical reactions between gases. In 1808 he stated the following law : *

When chemical changes occur between gases the volumes of the reacting gases and those of the products, if these are gaseous, are in the ratio of small whole numbers.

The same conditions of temperature and pressure are assumed.

It has been shown that 2 vols. of hydrogen and 1 vol. of oxygen give 2 vols. of steam (p. 37) and this and other experiments establish the following results :

2 vols. hydrogen + 1 vol. oxygen	= 2 vols. steam.
1 vol. hydrogen + 1 vol. chlorine	= 2 vols. hydrogen chloride.
1 vol. nitrogen + 3 vols. hydrogen	= 2 vols. ammonia.
1 vol. nitrogen + 1 vol. oxygen	= 2 vols. nitric oxide.
2 vols. nitrogen + 1 vol. oxygen	= 2 vols. nitrous oxide.
2 vols. carbon monoxide + 1 vol. oxygen	= 2 vols. carbon dioxide.
1 vol. carbon monoxide + 1 vol. chlorine	= 1 vol. carbonyl chloride.

Berzelius assumed that equal volumes of elementary gases contain equal numbers of *atoms*.

Let us see how this works out if we assume that the compound gas also contains in the same volume the same number of particles as the elementary gases. Let us represent the volumes by squares, which we may regard as sections of cubes containing equal volumes of gases. Take the case of hydrogen and chlorine and represent a hydrogen atom by ● and a chlorine atom by ○.

* See *Alembic Club Reprint* No. 4. Gay-Lussac's own words (published in 1809) are : " ces substances se combinent entre elles dans des rapports très-simples, et la contraction de volume qu'elles éprouvent par la combinaison suit aussi une loi régulière ".

We see from Fig. 48 that we cannot make the volumes right, because to do this hydrogen chloride would have to contain only half as many particles as an equal volume of hydrogen or chlorine. Dalton pointed

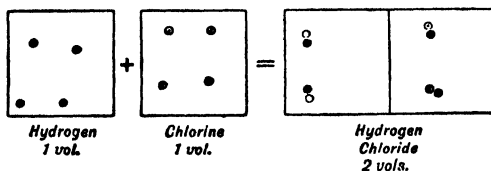


FIG. 48.—Combination of hydrogen and chlorine according to Berzelius.

out this difficulty. It was overcome by an Italian scientist Avogadro (1776-1856) in 1811.*

Avogadro's hypothesis.—Avogadro began by assuming that :

Equal volumes of all gases and vapours, under the same conditions of temperature and pressure, contain identical numbers of molecules.

A molecule is the smallest mass of a substance capable of existing in the free state.

The difficulty was now cleared away. Avogadro showed that it is necessary to assume that the particles of elementary gases are not atoms but are divisible molecules.

Let us assume that the molecules of hydrogen and chlorine each contain *two* atoms and that they are divided when the gases react. Then the volume relations will come out correctly, as we see from Fig. 49, and the formula of hydrogen chloride is found to be HCl :

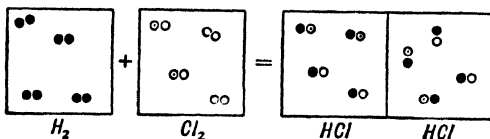
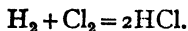


FIG. 49.—Combination of hydrogen and chlorine according to Avogadro.

In ordinary symbols :



Suppose one volume of hydrogen contains 100 molecules ; it reacts with an equal volume of chlorine, which Avogadro's hypothesis shows must also contain 100 molecules, to form *two* volumes of hydrogen chloride, which must contain 200 molecules. Each of these 200 molecules must contain at least one atom of hydrogen and one of chlorine, hence the

* See *Atombic Club Reprint* No. 4. Avogadro's own words are : "le nombre des molécules dans les gaz quelconques est toujours le même à volume égal . . . les rapports des masses des molécules sont alors les mêmes que ceux des densités des différents gaz, à pression et température égales". The memoir is in French.

100 molecules of hydrogen and the 100 of chlorine must have been divided into two parts, which we can suppose are the atoms.

Another example is the formation of steam from hydrogen and oxygen, and the formula of steam is seen to be H_2O :

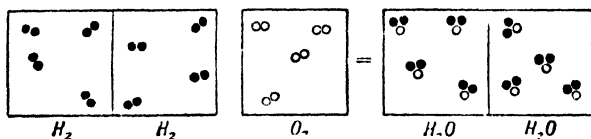


FIG. 50.—Combination of Hydrogen and Oxygen.

These formulae depend on the assumption that the molecules of hydrogen, oxygen and chlorine contain *two* atoms. This is the simplest assumption which explains the results, and we assume that it is the correct one.

There is some physical evidence, *e.g.* the value 1.4 for the specific heat ratio c_p/c_v (p. 89), that the molecules of hydrogen, oxygen, nitrogen and hydrogen chloride contain two atoms, or are *diatomic*. The number of atoms in a molecule of an element is called the *atomicity*. Mercury vapour and argon (Hg, A) are *monatomic*, ozone (O_3) is *triatomic*, phosphorus and arsenic vapour are *tetratomic* (P_4, As_4).

Molecular weight and density.—It follows from Avogadro's hypothesis (and was stated by him) that the weights of equal volumes of gases or vapours at the same temperature and pressure are in the ratio of the molecular weights.

The relative density (p. 64) of a gas (or vapour) is the ratio :

$$\frac{\text{weight of a given volume of the gas or vapour}}{\text{weight of an equal volume of hydrogen}}$$

at the same temperature and pressure.

Avogadro's hypothesis shows that the relative density is also equal to the ratio :

$$\frac{\text{weight of one molecule of the gas or vapour}}{\text{weight of one molecule of hydrogen}},$$

since equal volumes contain identical numbers of molecules.

If the atomic weight of hydrogen is taken as 1 the molecular weight is 2, since it has been shown that the hydrogen molecule contains 2 atoms ; hence the relative density of a gas is equal to :

$$\text{weight of one molecule (molecular weight)}$$

so that : molecular weight = relative density \times 2.

Actually, on the atomic weight standard oxygen = 16, the atomic weight of hydrogen is 1.008 and the molecular weight is 2.016 instead of 2.

Avogadro's hypothesis shows that a gram molecular weight (or mol) of *any* gas † at S.T.P. occupies the same volume. This is called the **gram molecular volume**, or **molar volume**.

Let M = molecular weight in grams of a gas, and D = normal density (weight of one litre at S.T.P.). Then :

$$\frac{M}{D} = \text{vol. of 1 mol in litres at S.T.P.} = V_m$$

For oxygen the molecule has been shown to contain two atoms each of weight 16; $\therefore M = 32$. It is found that $D = 1.429$ gm./lit., hence $V_m = 32/1.429 = 22.4$ litres. Avogadro's hypothesis shows that V_m is the same for all gases, hence

$$M = 22.4D.$$

The relative density is equal to the normal density divided by the normal density of hydrogen, viz. $D/0.09$, hence the normal density of a gas is the relative density multiplied by 0.09. Thus :

molecular weight = (rel. dens. $\times 0.09$) $\times 22.4$ = rel. dens. $\times 2.016$, as before.

Relative densities of gases were formerly referred to air = 1 as standard. The relative density of air = $1.2927 \div 0.08987 = 14.38$, hence the relative density referred to air = 1 is converted to that referred to hydrogen = 1 by multiplication by 14.38. The molecular weight ($O = 16$) is found by multiplying the density relative to air = 1 by 29.00, i.e. $14.38 \times 1.008 \times 2$.

***Limiting density.**—Since actual gases do not strictly obey Boyle's law, the density method gives only an approximate molecular weight when the gas is weighed at 0° and 1 atm. At very low pressures, however, gases obey Boyle's law and then equal volumes contain identical numbers of molecules.

Let p be the pressure in atm. and V lit. the corresponding volume at 0° of a mass W of gas. Then pV is not quite constant as p varies. By plotting pV against p a straight line is found for values of p less than 1 atm., and hence p_0V_0 , the value for $p = 0$, is found by extrapolation. This is the true value for Boyle's law.

It is found that

$$\frac{p_0V_0 - pV}{pV} = p\lambda;$$

$$1 + p\lambda = \frac{p_0V_0}{pV},$$

where λ is a constant (the **compressibility coefficient**) for each gas. If $p = 1$ atm. = p_1 , then $W/p_1V_1 = W/V_1$ = normal density, D . When p becomes

† Since vapours obey the gas laws *approximately* these statements hold approximately for vapours, it being assumed that they would follow the same laws when cooled to S.T.P. if this could be done.

zero, W/p_0V_0 is the density the gas would have if it obeyed Boyle's law, *i.e.* the limiting density, D_0 . Hence :

$$D_0 = D/(1 + \lambda),$$

or

$$\text{limiting density} = \text{normal density}/(1 + \lambda);$$

and the *exact* molecular weight is $22.42D_0$.

In this way some exact molecular, and thence atomic, weights have been found, and the method is at least as accurate as gravimetric analysis methods.

The general gas law.—On p. 61 it has been shown that for a given mass of an ideal gas the equation :

$$pv/T = \text{const.}, \text{ or } pv = \text{const. } T,$$

applies, where p = pressure, v = volume, T = absolute temperature. If the mass is 1 gm. mol. wt., or 1 mol, Avogadro's hypothesis shows that v is the same for all gases for the same values of p and T . This value of v has been shown to be 22.4 litres when $p = 1$ atm. and $T = 273$ (*i.e.* 0°C.). Hence the constant (which applies for all other values of p and T for 1 mol of gas and is denoted by R) is

$$R = 1 \times 22.4/273 = 0.082 \text{ litre atmospheres}/1^\circ \text{C.},$$

and

$$pv = RT.$$

R has the dimensions of energy divided by temperature, since (pressure \times volume) has the dimensions of work. In C.G.S. units the value of R , which is called the **gas constant**, is as follows :

$$p = 1 \text{ atm.} = 76 \times 13.596 = 1033.3 \text{ gm. wt. per sq. cm. (13.596 = density of mercury at } 0^\circ; 76 \text{ cm. of mercury at } 0^\circ = 1 \text{ atm. pressure);}$$

$$v = 22.4 \text{ lit.} = 22,400 \text{ c.c.}$$

$$\therefore R = 1033.3 \times 22,400/273 = 84,780 \text{ gm. cm.}/1^\circ.$$

If this is multiplied by 981, the gravitational acceleration, then 1033.3×981 is the atmospheric pressure in dynes per sq. cm., and

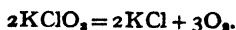
$$R = 84,780 \times 981 = 8.3 \times 10^7 \text{ ergs}/1^\circ.$$

Since 1 g. calorie = 4.18×10^7 ergs, the value of the gas constant in thermal units is $8.3 \times 10^7/4.18 \times 10^7 = 1.99$ g. cal./ 1° or practically 2 g. cal./ 1° .

Calculations of volumes of gases.—Avogadro's hypothesis shows that the molecular volume of *any* gas at S.T.P. is 22.4 litres. In calculations of volumes of gases, the chemical equations must be written so as to express reactions between *molecules* of the gases, since only in this case are the volume relations correctly given.

EXAMPLE 1.—Find the volume of oxygen, measured at 15° and 740 mm., evolved on heating 5 grams of potassium chlorate.

The equation is :



The molecular weight of KClO_3 is $39 + 35.5 + (3 \times 16) = 122.5$; \therefore 245 gm. of chlorate give 3×22.4 litres of oxygen at S.T.P. Hence 5 gm. of chlorate

give $\frac{5}{245} \times 3 \times 22.4$ litres at S.T.P.,

or $\frac{5}{245} \times 3 \times 22.4 \times \frac{760}{740} \times \frac{273 + 15}{273} = 1.49$ litres

at 15° and 740 mm. pressure.

EXAMPLE 2.—Find the weight of 1 litre of nitrogen at S.T.P.

The formula of nitrogen is N_2 , hence its molecular weight is $2 \times 14 = 28$. Therefore, since 1 molecular weight in grams, 28 grams, will occupy 22.4 litres at S.T.P., the weight of 1 litre at S.T.P. will be $28/22.4 = 1.250$ grams.

EXAMPLE 3.—Find the weight of 20 litres of carbon dioxide ($\text{CO}_2 = 44$) at 14°C . and 729 mm.

Vol. of 20 litres at S.T.P. $= 20 \times \frac{729}{760} \times \frac{273}{287} = 18.25$ litres.

Now 22.4 litres of carbon dioxide at S.T.P. weigh 44 gm.

\therefore weight of 18.25 litres at S.T.P. $= \frac{18.25}{22.4} \times 44 = 35.85$ grams.

Determination of vapour densities.—Three methods of determining the density of the vapour of a volatile liquid are used.

(1) In Dumas' method a thin glass bulb (Fig. 51) with a long neck is dried and weighed. By warming the bulb, dipping the neck in the liquid and cooling, sufficient liquid is introduced into the bulb to expel all the air when it is volatilised.

The bulb is supported in an iron pot containing water, oil or melted paraffin wax, heated at a known temperature above the boiling point of the liquid. Volatilisation rapidly occurs, the air being expelled through the tip of the bulb which projects above the surface of the liquid in the bath. When the rush of vapour ceases, the neck of the globe is sealed off, the barometric pressure is taken and the temperature of the bath is read off on the thermometer. The globe is taken from the bath, cooled, cleaned and reweighed along with the piece of neck sealed off. The neck is then scratched with a file and the tip broken off under water. The water rushes into the bulb and fills it completely. The bulb full of water is weighed.

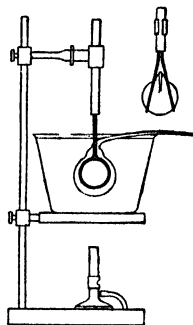


FIG. 51.—Dumas' vapour density apparatus.

The following example shows the method of calculation.

Vapour density of hexane.—Weight of empty globe in air = 23.449 gm.

Weight of globe + vapour at 15.5° = 23.720 gm.

Temperature of sealing = 110°.

Barometric pressure = 759 mm., unchanged throughout the experiment.

Capacity of globe, by weighing water = 178 c.c.

Weight of air displaced by globe

$$= 178 \times \frac{273}{288.5} \times \frac{759}{760} \times 0.001293 = 0.218 \text{ gm.}$$

(0.001293 gm. is the weight of 1 c.c. of air at S.T.P.)

∴ weight of *vacuous* globe = 23.449 - 0.218 = 23.231 gm.

∴ weight of vapour filling globe at 110° and 759 mm.

$$= 23.720 - 23.231 = 0.489 \text{ gm.}$$

The volume which the vapour would (theoretically) occupy at S.T.P.

$$= 178 \times \frac{273}{383} \times \frac{759}{760} = 126.7 \text{ c.c.} = 0.1267 \text{ litre;}$$

∴ normal density = 0.489/0.1267 = 3.86

∴ molecular weight = 3.86 × 22.4 = 86.5.

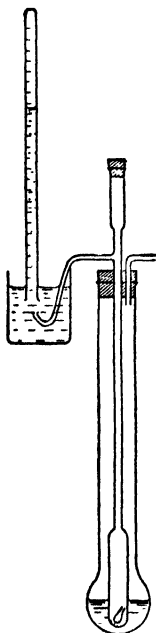


FIG. 52.—Victor Meyer's Vapour Density Apparatus.

(2) In Victor Meyer's method a long glass tube with a bulb (Fig. 52) and a side tube is heated in a glass (or better, copper) vapour bath at a temperature which must be constant and about 30° higher than the boiling point of the substance, but need not otherwise be known. The side tube delivers into a graduated tube in a trough of water. The long tube is heated in the bath until no more bubbles of air escape; then the side tube is placed under the graduated tube, the cork at the top of the long tube is taken out, and a weighed quantity of the liquid in a small stoppered bulb is dropped into the heated bulb, the cork being quickly replaced. A little glass wool or mercury is placed in the bottom of the bulb to prevent fracture on dropping in the bulb of liquid.

The substance quickly vaporises and the *vapour* (which does not diffuse to the top of the narrow tube) *displaces its own volume of air*, which is collected in the graduated tube. When no more bubbles come off, the water levels in the graduated tube and in a cylinder are equalised and the volume of air is read off. This is equal to the volume

which the vapour would occupy if it could be cooled to the temperature of the room.

EXAMPLE.—0.1008 gm. of chloroform expelled 20.0 c.c. of air at 15° and 757 mm. pressure.

$$\therefore \text{volume of air at S.T.P.} = 20 \times \frac{273}{288} \times \frac{757}{760} = 18.9 \text{ c.c.}$$

$$\therefore \text{normal density} = \frac{0.1008}{0.0189} = 5.33$$

$$\therefore \text{molecular weight} = 5.33 \times 22.4 = 119.3.$$

(3) In Hofmann's method a weighed amount of the liquid completely fills a small stoppered bottle which is pushed under the mercury in a rather wide barometer tube and rises into the vacuum on the top of the mercury. The barometer tube is surrounded by a glass jacket through which the vapour of a liquid is passed, the temperature being sufficiently high to vaporise the substance at the reduced pressure (Fig. 53). The temperature of the vapour jacket combined with the vacuum in the tube causes the liquid to vaporise and blow out the stopper of the bottle. The volume of vapour produced is read off at the temperature of the jacket. The pressure is the barometric pressure minus the height of the mercury column in the tube above the level of mercury in the bath. This method is capable of giving accurate results.

EXAMPLE.—0.338 gm. of carbon tetrachloride gave 109.8 c.c. of vapour; the temperature of the steam jacket was 99.5°, the barometric pressure 746.9 mm., and the height of the mercury in the tube above the level in the mercury bath 283.4 mm.

The volume of vapour at S.T.P.

$$= 109.8 \times \frac{(746.9 - 283.4)}{760} \times \frac{273}{372.5} = 49.1 \text{ c.c.}$$

\therefore normal density of carbon tetrachloride vapour

$$= \frac{0.338}{0.0491} = 6.88$$

$$\therefore \text{molecular weight} = 6.88 \times 22.4 = 154.1.$$

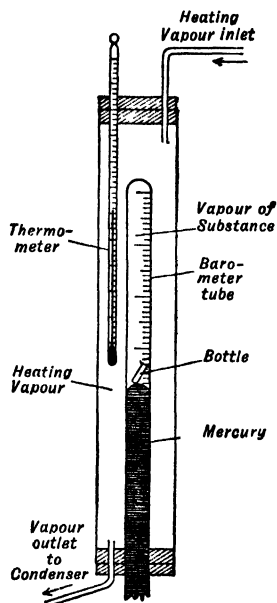


FIG. 53.—Hofmann's Vapour Density Apparatus.

The method of finding the density and hence the molecular weight of a gas by effusion is described in Chapter VII. Methods of finding molecular weights of dissolved substances are described in Chapter XVIII.

Cannizzaro's principle.—Cannizzaro * in 1858 explained how Avogadro's hypothesis can be used to find *atomic* weights.

(1) From vapour density measurements the *molecular weights* of a number of volatile compounds of the element are found.

(2) The analyses of these compounds give the weights of the element contained in the molecular weights of the compounds.

(3) The smallest of these weights is taken as the *atomic weight*, the assumption being made that at least one of the compounds contains only one atom of the element in its molecule.

The atomic weight of an element is the smallest weight of the element contained in a molecular weight of any of its compounds.

This may be called Cannizzaro's principle; it is not an independent definition of atomic weight, but follows from Avogadro's hypothesis.

It must be emphasised that the density of *one compound* of an element, or of *the element itself* if it is volatile, can give no sure indication of the atomic weight. The molecules of the particular compound selected, and those of the vapour of the free element, may contain one, two, three, or any number of atoms of the element, for all we know to the contrary. In the case of mercury, for example, the molecule in the vapour consists of *one* atom, and the molecule of phosphorus vapour contains *four* atoms. The larger the number of compounds taken the more likely it is that one will contain only one atom of the element in a molecule.

OXYGEN COMPOUNDS

Compound	Vap. density (H = 1) Δ	Mol. wt. $= 2 \times \Delta$	Wt. of oxygen in one mol. wt. of compound
Oxygen gas - - -	16	32	16×2
Water - - - - -	9	18	16
Carbon monoxide - - -	14	28	16
Carbon dioxide - - -	22	44	16×2
Sulphur dioxide - - -	32	64	16×2
Sulphur trioxide - - -	40	80	16×3
Nitrous oxide - - -	22	44	16
Nitric oxide - - -	15	30	16

The least weight of oxygen found in a molecular weight of any one of these compounds is 16, and this is taken as the atomic weight of oxygen.

A molecule of water contains one atom of oxygen of weight 16, and hence $18 - 16 = 2$ parts, or two atoms, of hydrogen. Hence the formula is H_2O .

* *Alambic Club Reprint* No. 18. See Tilden, Memorial Lecture on Cannizzaro, *Chemical Society Memorial Lectures*, vol. 2 (1914).

Confirmation of atomic weights.—The atomic weights thus found by Cannizzaro's principle from vapour densities have been confirmed by several independent methods. These remove the possibility that the least weight of an element found in the molecular weights of all the compounds examined may still be a multiple of the atomic weight, since it is very improbable that *all* the independent methods should agree with this particular multiple. These methods are :

1. Molecular weights of substances in solution found by osmotic pressure, freezing point, boiling point or vapour pressure methods usually agree with those found from vapour densities. In some cases, *e.g.* metals in amalgams, the molecular weight is identical with the *atomic* weight.

2. The ratio of the specific heats of a gas or vapour at constant pressure c_p , and at constant volume c_v , viz. c_p/c_v , according to the kinetic theory of gases, has the value 1.667 when the molecule is *monatomic*. In 1876 Kundt and Warburg found that $c_p/c_v = 1.667$ for mercury vapour, hence the molecules of the latter consist of single atoms. The density of mercury vapour shows that the molecular weight is 200. This in the present case is equal to the atomic weight. If the atomic weight found by the vapour density method is shown in one case, viz. mercury, to be the real atomic weight and not a multiple, it may reasonably be assumed that in other cases also the method gives the real atomic weights. In the case of many *diatomic* gases, the theoretical ratio $c_p/c_v = 1.4$ is also found.

3. Dulong and Petit in 1819 found that the product of the atomic weight and the specific heat of a solid element is approximately constant and equal to 6.3. Hence if the specific heat of a solid element is determined, and 6.3 is divided by this number, we obtain an *approximate* value of the atomic weight. This does not give correct results with elements of small atomic weight.

4. Mitscherlich in 1819 found that compounds having analogous formulae crystallise in the same form or are isomorphous. Thus the formulae of isomorphous compounds can be found and hence, by analysis, the atomic weights of their elements.

In some cases a substance may crystallise in more than one form, and this must be kept in mind in using the method.

5. The formulae of compounds which show similarities in chemical properties are usually similar. Oxides of iron, aluminium and chromium are given similar formulae, Fe_2O_3 , Al_2O_3 and Cr_2O_3 . If the atomic weight of chromium is found those of aluminium and iron can be determined. This method is the least trustworthy of all those described ; *e.g.* beryllium oxide was long thought to be Be_2O_3 instead of BeO on the basis of chemical analogies.

6. The position of an element in the Periodic System (p. 250) shows that its atomic weight has been correctly chosen.

In some cases volatile compounds of an element are not known or are too unstable for vapour density measurements or else volatilise only at

very high temperatures. In this case, the atomic weight must be found by the methods given above.

Dulong and Petit's law.—A useful check on the atomic weights of *solid* elements is given by the law of Dulong and Petit. The unit of heat, the calorie, is the amount of heat required to raise the temperature of one gram of water through 1°C . The specific heat of a substance is the number of calories required to raise the temperature of one gram of the substance through 1°C .

The atomic weight of a solid element multiplied by its specific heat is almost the same for all elements and is approximately equal to 6.3.

The number of calories required to raise the temperature of the atomic weight in grams of a solid element through 1°C . is called the atomic heat. Thus, for solid elements :

$$\text{atomic weight} \times \text{specific heat} = \text{atomic heat} = 6.3.$$

Element	Atomic weight <i>A</i>	Specific heat <i>C</i>	Atomic heat <i>AC</i>
Copper - - - -	63.5	0.09	5.9
Iron - - - -	56	0.11	6.1
Lead - - - -	207	0.03	6.41
Iodine - - - -	127	0.0524	6.64
Mercury (solid) - - -	200.6	0.033	6.7
Phosphorus (white) - -	31	0.198	6.2
Sulphur - - - -	32	0.175	5.6
Zinc - - - -	65.5	0.094	6.2

As Dulong and Petit expressed it, all atoms of solid elements have the same capacity for heat. Thus if we determine the specific heat of a solid element and divide 6.3 by this specific heat we obtain the *approximate* atomic weight. By comparing this with the exact equivalent found by chemical analysis, say of the chloride of the element, we find which multiple of the equivalent is equal to the *exact* atomic weight.

It must be noted that *certain elements of small atomic weight show deviations from Dulong and Petit's law*. Their atomic heats are *smaller* than 6.3, *e.g.* those of carbon (1.9), boron (2.6) and silicon (4.8). At higher temperatures, however, these atomic heats tend to become normal, as is seen from the following table :

Element	Temperature	Atomic heat
Carbon - - - -	980°	5.6
Boron - - - -	233°	4.3
Silicon - - - -	232°	5.68

At very low temperatures the atomic heats of *all* elements become small and in some cases very small (Fig. 54). In the case of diamond the atomic heat has vanished at the temperature of liquid hydrogen (-253°). This

is explained by Planck's quantum theory, according to which energy is taken up discontinuously by atoms of solids in multiples of a quantum $h\nu$, where h is Planck's constant and ν is a frequency which varies from element to element; ν is small for elements which obey Dulong and Petit's law.

It was found experimentally by Joule that *the molecular heat of a compound* (= molecular weight \times specific heat) *is the sum of the atomic heats of its elements*. For example, the specific heat of lead iodide PbI_2 is 0.0427. The molecular weight is $207 + (2 \times 127) = 461$, hence the molecular heat is $461 \times 0.0427 = 19.68$. The sum of the atomic heats is $6.41 + (2 \times 6.64) = 19.69$.

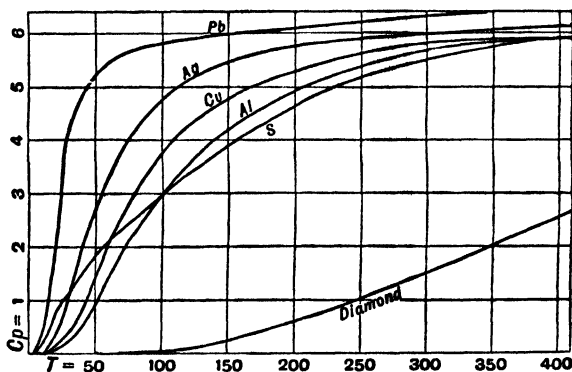


FIG. 54.—Atomic heats at low temperatures.

In this way the atomic heats of elements like oxygen and chlorine may be calculated for the state in which they exist in solid compounds.

As an example of the application of atomic heats to the determination of atomic weights, consider the case of tin. This forms with chlorine a volatile liquid stannic chloride, the vapour density of which is 132.9, hence the *approximate* molecular weight is $132.9 \times 2 = 265.8$. By *exact* analysis it is found that the compound contains in percentages: tin 45.6, chlorine 54.4.

The amount of chlorine in 265.8 parts of stannic chloride is

$$54.4 \times 265.8 \div 100 = 144.6.$$

This, however, is approximately $4 \times 35.5 = 142.0$, and hence we may assume that the molecule of stannic chloride contains four atoms of chlorine, or the formula is Sn_2Cl_4 . To find x we require additional information. Now the specific heat of tin is 0.056, hence the *approximate atomic weight* of tin is $6.3 \div 0.056 = 113$.

From the *exact* analysis of the compound, however, we find that the amount of tin combined with four atoms of chlorine is

$$45.6 \times 142.0 \div 54.4 = 119.$$

By comparison with 113 we conclude that 119 is the *exact atomic weight* of tin, so that stannic chloride contains one atom of tin ($x=1$) and its formula is SnCl_4 .

An alternative method of calculation is the following :

The *equivalent* of tin in stannic chloride is the weight combining with 35.5 parts of chlorine :

$$= 45.6 \times \frac{35.5}{54.4} = 29.75.$$

The approximate atomic weight of tin, by Dulong and Petit's law, is :

$$\frac{6.3}{0.056} = 113.$$

The valency of tin in stannic chloride is (p. 79) :

$$\frac{\text{atomic weight}}{\text{equivalent}} = \frac{113}{29.75} = 3.8.$$

But the valency must be a whole number, in this case 4, hence :

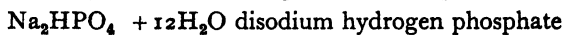
$$\text{atomic weight of tin} = 29.75 \times 4 = 119.0.$$

Isomorphism.—In 1819, the same year in which Dulong and Petit announced their law, Eilhard Mitscherlich published a memoir : " On



FIG. 55.—Isomorphous crystals of common alum and chrome alum (right).

the relation which exists between the crystalline form and chemical proportions". He found that phosphates and arsenates of similar composition and containing the same amount of water of crystallisation had almost exactly the same crystalline form : *e.g.* the two compounds



both crystallise in the same monoclinic form.

The capacity of different but chemically similar substances of crystallising in the same form was called by Mitscherlich **isomorphism** ; substances crystallising in the same form are called **isomorphous**. Other examples of isomorphous substances are common alum $\text{K}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$ and chrome alum $\text{K}_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$ (Fig. 55).

Chrome alum contains 10.42 per cent. of chromium and 7.82 per cent. of potassium. From the formula we see that the atomic weight of chromium is the weight contained in such a weight of chrome alum as contains an atomic weight (39) of potassium, i.e. $\frac{100 \times 39}{7.82} = 498.8$ parts of chrome alum;

$$\therefore \text{atomic weight of chromium} = 10.42 \times \frac{498.8}{100} = 52.$$

This is confirmed by the specific heat of chromium = 0.124

$$\therefore \text{approximate atomic weight} = \frac{6.3}{0.124} = 51.$$

Mixtures of isomorphous substances cannot be completely separated into their pure components by ordinary crystallisation, since the crystals separating contain both substances. For example, when a solution containing common alum and chrome alum is crystallised the crystals all contain both alums. Hence they are sometimes called *mixed crystals*. Since they are not mechanical mixtures but are homogeneous, the name *solid solutions* is preferable.

If an octahedral crystal of chrome alum is suspended by a thread in a saturated solution of potash alum, a colourless overgrowth of the latter salt is deposited on the violet crystal as nucleus. Similarly, a green crystal of nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, may be covered with a colourless crystal of magnesium sulphate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The property of forming such *layer crystals* or *overgrowth crystals* is shown by isomorphous substances.

Isomorphous substances therefore generally (1) crystallise in the same form; (2) form solid solutions; (3) form overgrowth crystals.

The variable composition of minerals containing isomorphous elements is represented by such formulae as $(\text{Ni}, \text{Cu}, \text{Fe})\text{S}$, which is a native sulphide of nickel in which some nickel is replaced by copper and iron.

In some cases a substance may crystallise in two different forms, when it is called *dimorphous*, and only one form and perhaps not the common one is isomorphous with a chemically similar substance. An example of this was discovered by Mitscherlich in the compounds $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$.

In some cases compounds containing the same number of atoms but not otherwise chemically similar are isomorphous:

Potassium perchlorate	KClO_4	Potassium sulphate	K_2SO_4
Barium sulphate	BaSO_4	Potassium beryllium	
Potassium fluoborate	KBF_4	fluoride	K_2BeF_4

The structure of crystals.—The outward shapes of crystals correspond with an orderly internal arrangement of the atoms and molecules com-

posing them. Just as the shape of a house depends on the careful arrangement of the bricks or blocks of stone from which it has been built according to some definite plan, so the shape of a crystal depends on a definite arrangement of the atoms or molecules which form its structural units. In recent years this interior structure of crystals has been explored by means of the X-rays.

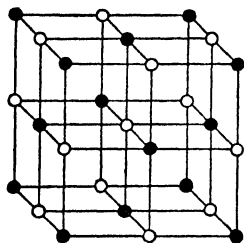


FIG. 56.—Lattice of rock salt.

X-rays, which are of wave-lengths not much longer than the diameters of atoms (10^{-8} cm.), are deviated by the separate atoms in the crystal or even in a powdered crystal. The rays passing through when allowed to fall on a photographic plate form a definite pattern of lines or spots corresponding with an X-ray spectrum. From the nature of this spectrum the arrangement of the atoms in the crystal may be calculated.

The atoms in a crystal are built up into a **lattice** or mass-produced pattern repeated over and over again, each little pattern being called a **unit cell**. Fig. 56 shows the lattice arrangement of rock-salt, the centres of the chlorine and sodium atoms being shown (really the electrically charged chlorine and sodium *ions*, p. 198). There are no molecules of NaCl as such in the crystal, but only independent ions in a cubic lattice. The spherical ions are close packed, and in contact. Fig. 57 shows the lattice of the Iceland spar: here the calcium atoms (ions) and the CO_3 radicals form the structural units. Each carbon atom is associated with three oxygen atoms arranged symmetrically around it in a plane, so that the carbonate radical CO_3 preserves an independent existence in the crystal.

Dissociation.—Avogadro's hypothesis applies to mixed as well as to pure gases; the *total* number of molecules in a given volume of air is the same as the number of molecules in an equal volume of pure oxygen or nitrogen at the same temperature and pressure.

When Avogadro's hypothesis was first used to find molecular weights some apparent exceptions were noticed, *e.g.* with ammonium chloride, phosphorus pentachloride and sulphuric acid.

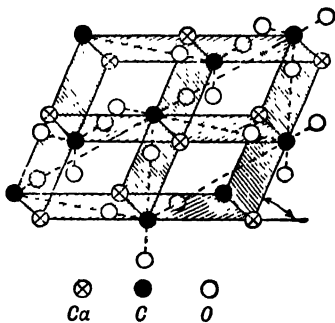


FIG. 57.—Lattice of calcite.

The simplest formula of ammonium chloride is NH_4Cl , with a molecular weight 53.5. Bineau found the vapour density to be 12.9, corresponding with a molecular weight of 25.8, or about half the theoretical value and corresponding with the formula $\text{N}\frac{1}{2}\text{H}_2\text{Cl}\frac{1}{2}$. This led Deville to question the validity of Avogadro's hypothesis.

The true explanation was put forward independently by Cannizzaro in 1857, and by Kopp and Kekulé in 1858.

They assumed that ammonium chloride on heating breaks up into ammonia and hydrogen chloride :



which recombine on cooling. The density would then, for complete decomposition, be half the theoretical density, because the decomposed gas occupies double the volume it would if no decomposition had taken place. *When a substance decomposes on heating and the products recombine on cooling, the process is called dissociation.*

Pebal in 1862 was able to prove that dissociation takes place by separating ammonia and hydrochloric acid from the vapour by diffusion. Ammonia is much lighter than hydrochloric acid and therefore diffuses more rapidly. According to Graham's law (p. 66), the relative rates of diffusion will be :

$$\frac{\sqrt{36.5}}{\sqrt{17}} = 1.47.$$

This may be shown by the following experiment.

Some ammonium chloride is put into a glass tube through which passes a porous clay tobacco-pipe stem (Fig. 58). On heating the

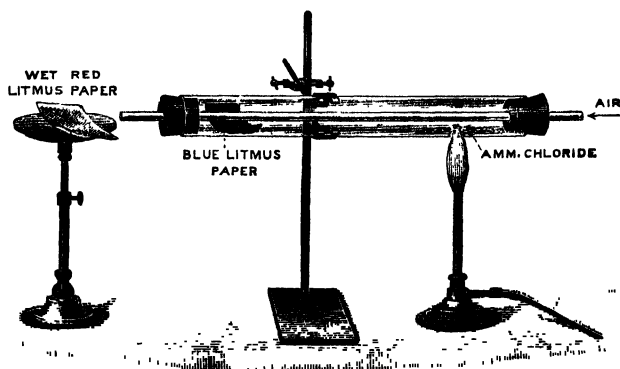
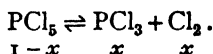


FIG. 58.—Dissociation of ammonium chloride.

ammonium chloride dissociates into ammonia and hydrogen chloride gases. The ammonia diffuses more rapidly through the porous tube, leaving in the glass tube an excess of hydrogen chloride which reddens

a piece of blue litmus paper. By passing a *slow* current of air through the clay tube, the gas containing excess of ammonia is directed on a piece of moist red litmus paper which becomes blue.

In many cases the dissociation is incomplete, *i.e.* some of the original substance is present as well as the products of its dissociation and a state of **chemical equilibrium** (p. 49) results. This happens, for example, with phosphorus pentachloride, which dissociates into phosphorus trichloride and chlorine :



Let 1 gm. molecule of PCl_5 be taken and let x gm. molecules of it be dissociated, then x gm. molecules of PCl_3 and Cl_2 will be formed. There will be $1-x$ gm. molecules of PCl_5 undissociated. The number of gm. molecules in the partly dissociated gas will be $1-x+x=1+x$.

The volumes are proportional to the numbers of molecules, by Avogadro's hypothesis, hence the volume, V' , is $1+x$ times the volume, V , which would be occupied by the PCl_5 if it were not dissociated. The densities are inversely proportional to the volumes, since in each case

$$\text{density} \times \text{volume} = \text{mass},$$

and the same total mass of substance is present. Let D be the (theoretical) density of PCl_5 and D' the observed density of the gas, then :

$$\frac{V'}{V} = \frac{D}{D'} = 1+x.$$

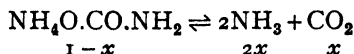
From this equation the value of x , the *extent of dissociation*, may be calculated.

At 200° the vapour density ($H=1$) of phosphorus pentachloride is 70. The theoretical vapour density of PCl_5 is 104.25. Thus

$$1+x = \frac{104.25}{70} = 1.486; \quad \therefore x = 0.486,$$

i.e. 48.6 per cent. of the PCl_5 molecules are dissociated at 200° .

If 1 molecule of substance dissociates into more than 2 molecules, the calculation must be suitably modified. *E.g.* with ammonium carbamate (p. 301) :



the number of gm. mols. formed from 1 gm. mol. is $1+2x$;

$$\therefore \frac{D}{D'} = 1+2x.$$

The kinetic theory of gases.—The properties of gases (Boyle's law ; expansion by heat ; diffusion) are all explained by the kinetic theory of gases, developed mainly in the nineteenth century. The fact that a liquefied gas occupies only a small fraction of the bulk of the gas proves

that *the molecules in a gas are widely separated*. When a gas is compressed the molecules are brought closer together.

Liquids and solids are compressed only slightly even by very large forces. Their molecules are closely packed with only a small amount of free space. Since the molecules of solids and liquids, unlike those of gases, do not tend to separate and spread through any volume available to them, they are supposed to be held together by an attractive force called cohesion. In gases there is very little cohesion between the molecules unless they are fairly close together, as when the gas is strongly compressed and when the molecules may then form a liquid.

The molecules of a gas do not tend to settle out on standing and the mixing or diffusion of gases shows that *the molecules of a gas are in motion*.

The pressure of a gas on a containing vessel is due to the bombardment of the walls of the vessel by the gas molecules. The molecules must be perfectly elastic, so that they rebound on striking the wall or on colliding with one another, with undiminished kinetic energy. If they were not elastic they would gradually come to rest and the pressure would vanish.

When a gas is compressed its molecules are crowded together so that there is a greater number in a given space. Their speeds are not altered if the temperature remains the same. The particles will collide more often with the walls of the vessel and the pressure will increase. The diagrams of Fig. 59 show that when the volume is reduced to one-half and one-quarter, respectively, there will be twice and four times the number of molecules in a given space, and thus there will be twice or four times the number of collisions per second as in the gas at the original volume. *The pressure is therefore inversely proportional to the volume*, as Boyle's law requires. This result was deduced by Bernoulli in 1738.

If a gas is heated in a vessel so that the volume remains constant, the pressure increases. Since the number of molecules remains the same per unit volume, their speed must have increased so as to produce more collisions per second, and as the velocity is larger the momentum (mass \times velocity) of the particles is increased and the violence of each collision is greater. Heat is a form of kinetic energy and when a gas is heated whilst its volume remains constant, the heat absorbed goes to increase the kinetic energy of each particle of the gas. The kinetic energy of a molecule of mass m is $\frac{1}{2}mv^2$, where v is the velocity. The temperature is a measure of the mean kinetic energy of the molecules. At the absolute zero the molecules would have no kinetic energy and the pressure would be zero.

Suppose n molecules each of mass m of a gas are contained in a centimetre cube and let the mean velocity of the molecules be u . Each

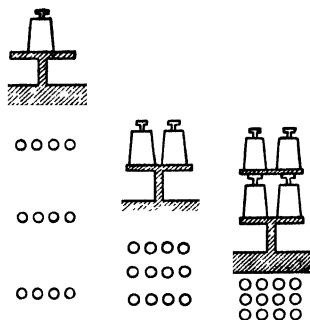


FIG. 59.—Compression of a gas : Boyle's law.

molecule collides u times per second with a cube face and its momentum changes from mu to $-mu$, *i.e.* the change of momentum per second is $2mu$. We can consider $\frac{1}{3}$ of the molecules moving between each pair of faces, hence the change of momentum per second for *one* face is $\frac{1}{3}mnu^2$, and this is equal to the force exerted on the 1 sq. cm. face, *i.e.* the pressure of the gas, p . Hence :

$$p = \frac{1}{3}mnu^2 = \frac{1}{3}\rho u^2,$$

where ρ = density = mass per c.c. (= mn). This is equivalent to Boyle's Law.

The absolute temperature T is proportional to the kinetic energy of the molecules, *i.e.* to $\frac{1}{2}mu^2$, hence it follows that :

$$p = \text{const.} \times T,$$

which is equivalent to Charles's Law.

If equal volumes of two gases at the same temperature and pressure contain n_1 and n_2 molecules of masses m_1 and m_2 , respectively, we have :

$$p = \frac{1}{3}m_1n_1u_1^2 = \frac{1}{3}m_2n_2u_2^2 \text{ (pressures equal)}$$

and

$$\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2 \text{ (temperatures equal),}$$

hence

$$n_1 = n_2,$$

which is Avogadro's Hypothesis.

If we have two gases at the same temperature and the same pressure, the kinetic energies of their molecules will be equal. Thus

$$\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2; \therefore u_1/u_2 = \sqrt{m_2/m_1},$$

i.e. the velocities of the molecules are inversely proportional to the square roots of the molecular weights, *i.e.* of the densities. The velocity of diffusion, however, is clearly proportional to the velocity of the molecules, hence Graham's Law (p. 66) results.

Velocity and free path of gas molecules.—Since the particles of a gas are acted upon by gravity, there will be a tendency for them to settle to the lowest part of the gas, but in a small volume of gas this is almost completely overcome by the motion of the molecules. In a very tall column of gas there is an appreciable settling out due to gravity, and this is why the atmosphere becomes more and more rarefied as we ascend from the surface of the earth. In a mixture of gases there will also be a tendency for the heavier molecules to cluster together nearer the bottom of the column and the lighter at the top, so that in the upper layers of the atmosphere there is probably more nitrogen than in the lower parts, which contain relatively more oxygen. This difference in composition is found only at great heights, where the atmosphere is not mixed by air currents.

The velocity of gaseous molecules depends, at a given temperature, on the mass of the molecules, and since the mean kinetic energy is the same, the heavier molecules move more slowly than the lighter. In oxygen (or air) at the ordinary temperature, the molecules are darting about with speeds of about a mile a second, *i.e.* about as fast as a rifle bullet. This is easily calculated from the formula $p = \frac{1}{3}\rho u^2$. Each

particle moves in a straight line until it collides with another particle or with the walls of the vessel, when it starts off in a straight line in another direction. The *average distance* through which a molecule moves between a collision with another molecule and the next collision is called the **mean free path**. It depends on the pressure, and is smaller the higher the pressure, since the molecules are then closer together. In air at atmospheric pressure the mean free path is only about a ten thousandth of a millimetre (10^{-5} cm.). If all the free paths of an oxygen molecule are joined so as to make up 1 mile, which is the distance traversed per second, 4000 million of them (4×10^9) will be required, and this gives the number of collisions per second.

Energy of gas molecules.—The heat supplied to a gas will generally be used partly to increase the kinetic energy of the molecules due to their *motion in straight lines*. This is the only effect when the molecules consist of single atoms, as in mercury vapour and argon which are monatomic gases, and is the only part of the kinetic energy concerned with the pressure of the gas. Part of the energy supplied will increase the kinetic energy due to the *rotation* of the molecules. For example, a molecule of hydrogen, oxygen, etc., composed of two atoms may be pictured as a very minute rotating dumb-bell. In more complicated molecules the atoms may also vibrate, like two balls connected by a spring, and this *vibration* will also absorb kinetic energy. All these contributions go to make up the heat energy of a gas. It is obvious that we can obtain some idea of the complexity of the molecules of a gas from its *specific heat*, the energy absorbed per gm. per 1° rise in temperature.

In practice, the *ratio of specific heats*, c_p/c_v , is used. For monatomic gases this is 1.666, for rigid diatomic molecules (O_2, N_2) it is 1.4, and for more complicated molecules it is still smaller.

The molecular structure of liquids.—The molecules of liquids are closer together than in a gas and are practically in contact. Diffusion takes place in liquids as in gases. This can be shown by placing some crystals of a coloured salt such as copper sulphate at the bottom of a tall cylinder of water and noting that the colour due to the dissolved substance slowly rises through the column of water. The molecules in the liquid are therefore in motion.

When a liquid is heated, some molecules get so much kinetic energy that they break away from the attraction of the other molecules in the liquid and start on a voyage through the space above the liquid. They have now become gas molecules and this is what happens in the evaporation of a liquid.

When a molecule of vapour approaching the liquid comes near it, the attractive force asserts itself and the molecule is dragged into the liquid. This is condensation. When as many molecules enter as leave the liquid in a given time, there is equilibrium and the vapour is then saturated.

Counting and weighing atoms and molecules.—Although Dalton's atomic theory, Avogadro's hypothesis and the kinetic theory of gases were used by chemists and physicists throughout the nineteenth century, and although calculations of the number of molecules in 1 c.c. of a gas by different methods had given results in good agreement, some chemists

were inclined to insist on the hypothetical character of the atomic theory. With the opening of the twentieth century methods of detecting the effects of single atoms were evolved.

This became possible with the discovery of radium by Madame Curie and the study of radioactivity. The atom of radium differs from atoms such as oxygen in being unstable. It can undergo a change in which it breaks down and the tiny fragments of the exploded atom are projected with immense velocities. One of these fragments is the α -particle, which is a positively charged helium atom possessing great kinetic energy. When α -particles pass in straight lines through a gas they collide with the atoms of the gas and eject the outer electrons of the atoms. These electrons and the positively charged residues of the atoms make the gas a conductor of electricity, since they can move under the influence of an electric field. If the conducting effect is amplified, the presence of a single α -particle can be detected. In this way the α -particles may be counted. This method was used by Rutherford and Geiger in 1908.

Their apparatus consisted of a long exhausted glass tube AA' (450 cm. long and 2.5 cm. wide) (Fig. 60), which contained on a lead plate a at

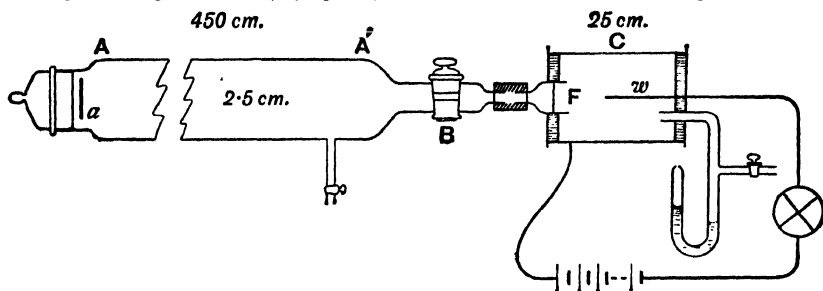


FIG. 60.—Rutherford and Geiger's experiment.

the end A a preparation of radium, which expelled α -particles. Some of these shot along the tube and passed through the narrow tube B into the brass chamber C , where the gas at low pressure was rendered conducting. A mica window at F shut off the gas from the evacuated tube AA' . Running through the vessel C and insulated from it by the ebonite ends was a metal wire w which was connected through a battery and electrometer to the outer surface of the brass vessel. As each α -particle entered the chamber (at the rate of about one every second) it made the gas conducting and the electrometer gave a deflection. In this way the individual α -particles passing into C could be counted. Since it was shown by separate experiments that α -particles turn into helium gas, and since the volume of helium gas given off by the radium preparation in a given time could also be found by experiment, all the data required were known.* We have simply to find how many α -particles would go to form

* Allowance is made of course for the fact that only a small, calculable fraction of the α -particles emitted by a pass through F .

22.4 litres of helium at S.T.P., and this gives us the number of molecules in a gram molecule.*

The number of molecules in a gram molecule, called *Avogadro's constant*, is thus found to be 6×10^{23} . This corresponds with 3×10^{19} molecules per c.c. of a gas at S.T.P. If we imagine the molecules in this 1 c.c. of gas passing out one by one through a small aperture at the rate of one million per second, it would then take one million years for them all to pass out.

Molecules are extremely minute; the diameter of the hydrogen molecule is about 2×10^{-8} cm. The smallest distance which can be perceived with a powerful microscope is about 0.0002 mm., and it is surprising that this would contain only about 1000 hydrogen molecules placed in line. If we could increase the power of the best microscope rather less than a thousand-fold, we should see large molecules quite easily provided the usual laws of optics held good.

We can now calculate *the weight of an atom of hydrogen*. Two grams of hydrogen contain 6×10^{23} molecules, each containing two atoms. Hence each atom weighs

$$1 \div 6 \times 10^{23} \text{ gm.} = 1.66 \times 10^{-24} \text{ gram.}$$

To find the weight of any other atom or molecule we multiply this number by the atomic or molecular weight of the substance.

* The accepted values are :

for Avogadro's constant $N = 6.024 \times 10^{23}$,
the electronic charge $e = 4.802 \times 10^{-10}$ e.s.u.,
and Planck's constant $h = 6.623 \times 10^{-27}$.

CHAPTER X

VALENCY

Valency.—Hydrogen compounds are known in which one atom of an element is combined with one, two, three, or four atoms of hydrogen :

HCl	H_2O	H_3N	H_4C
Hydrochloric acid.	Water.	Ammonia.	Methane.

The atoms of chlorine, oxygen, nitrogen, and carbon can unite with one, two, three, and four atoms of hydrogen, respectively. None of these compounds of hydrogen contains more than one atom of an element combined with one atom of hydrogen, and the latter is therefore taken as the standard of combining capacity or valency.* *The valency of an element is measured by the number of hydrogen atoms which unite with one atom of that element.* The elements chlorine, oxygen, nitrogen, and carbon are univalent, bivalent, trivalent, and quadrivalent respectively.†

Since chlorine is univalent it may be used instead of hydrogen in determining the valencies of elements, which are the same as those referred to hydrogen, but quinquevalent elements are now included :

Cl_2O	Cl_3N	Cl_4C	Cl_5P
Chlorine monoxide.	Nitrogen trichloride.	Carbon tetrachloride.	Phosphorus pentachloride.

Oxygen is bivalent and if it combines with one atom of another element the latter (*e.g.* calcium in calcium oxide CaO) is also bivalent and will combine with two atoms of hydrogen (CaH_2) or chlorine (CaCl_2). In

* The only case in which 1 atom of hydrogen combines with more than 1 atom of another element is hydrazoic acid HN_3 in which the azide group $-\text{N}_3$ is univalent.

† The hybrid names *mono-, di-, tri-, tetra- and penta-*valent are often used instead of the more correct *uni-, bi-, ter-, quadri- and quinque-*valent. In this book the convenient abbreviations 2-, 3-, 4-, 5-, 6-, 7- and 8-valent will be commonly used. The valency of an element is often denoted by a Roman numeral above the symbol : $\overset{\text{III}}{\text{N}}, \overset{\text{V}}{\text{P}}$.

oxygen compounds additional valencies, 6, 7 and 8, appear, the highest valency known being 8 :

Na_2O Sodium monoxide.	CaO Calcium oxide.	Al_2O_3 Aluminium oxide.	CO_2 Carbon dioxide.
P_2O_5 Phosphorus pentoxide.	SO_3 Sulphur trioxide.	Cl_2O_7 Chlorine heptoxide.	OsO_4 Osmium tetroxide.

Chlorine is 7-valent and osmium is 8-valent in their highest oxides.

An element may have a *variable* valency either in its compounds with the *same* element, or in its compounds with *different* elements :

PCl_3 (3)	SO_2 (4)	PH_3 (3)	SH_2 (2)
PCl_5 (5)	SO_3 (6)	P_2O_5 (5)	SF_6 (6)

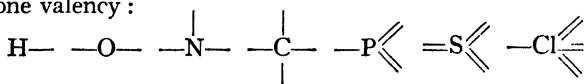
The *equivalent* is the weight of an element which combines with or displaces unit weight of hydrogen. But the valency is the number of unit weights (atoms) of hydrogen which combine with, or are displaced by, one atomic weight of the element. Hence :

Atomic weight = Equivalent \times Valency, or

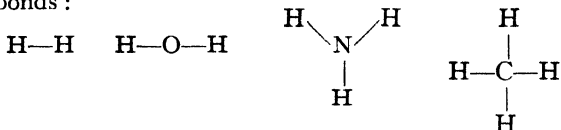
$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent}}.$$

The idea of *valency* or *combining capacity* is due to Edward Frankland (1852).

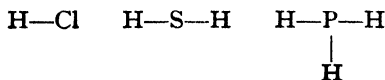
Structural formulae.—We may form a picture of the combination of atoms by assuming that each combined atom has one or more **bonds**, shown by straight lines drawn from the symbol of the atom, each bond representing one valency :



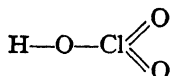
In the molecules of compounds these bonds are united in pairs. In writing the formulae of the compounds, the pairs of bonds are contracted to single bonds :



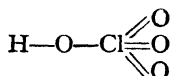
Higher valencies of elements.—The elements chlorine, sulphur and phosphorus show valencies of one, two and three in simple compounds with hydrogen :



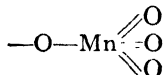
In the oxy-acids of these elements the atoms show higher valencies. The formula of chloric acid, for example, which forms salts such as potassium chlorate, is written :



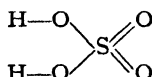
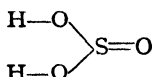
in which chlorine is 5-valent, and the formula of perchloric acid is :



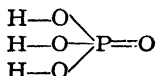
in which chlorine is 7-valent. A similar formula is assumed for the permanganate radical,* in which manganese, which is bivalent in simple compounds such as MnCl_2 and MnSO_4 , is now 7-valent :



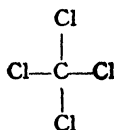
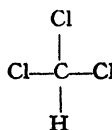
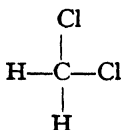
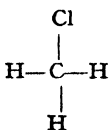
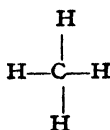
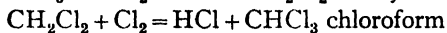
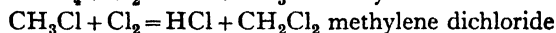
The formulae of sulphur dioxide and trioxide may be written so as to make sulphur 4-valent and 6-valent, respectively, and sulphur may be supposed to have these valencies in sulphurous and sulphuric acids :



In phosphoric acid the phosphorus may be regarded as 5-valent :



Saturated and unsaturated compounds.—Since in methane CH_4 all the valencies of the carbon are united with hydrogen, chlorine can react only by turning out the hydrogen (as hydrochloric acid) and taking its place—a so-called substitution reaction (p. 23). Four compounds are produced :



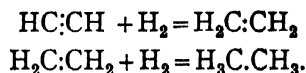
* The permanganates actually consist of two separate *ions*, K^+ and MnO_4^- , and the valency of Mn in the ion is 7.

In some cases *two* or more valencies of an atom of an element can unite with a corresponding number of valencies of an atom of the *same* element :

- | | | |
|--------------|--|--|
| 1. Ethane | $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ | single bond, or linkage, between carbon atoms. |
| 2. Ethylene | $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ | double bond, or linkage, between carbon atoms. |
| 3. Acetylene | $\text{H}-\text{C}\equiv\text{C}-\text{H}$ | triple bond, or linkage, between carbon atoms. |

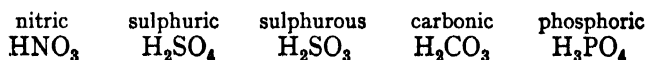
Such double and triple bonds are often represented by dots.

Molecules of compounds with multiple bonds are *unsaturated*, *i.e.* can add on other atoms to form saturated compounds which react only by substitution :

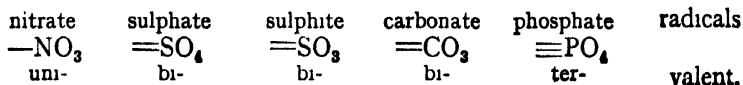


Valencies of radicals.—The idea of valency may be extended to radicals. Molecules such as O_2 , H_2O and CO_2 , in which the valencies of the elements are balanced, are called *saturated*. Radicals are parts of saturated molecules, they possess valency, and do not ordinarily occur in the free state. Water may be regarded as a compound of the hydrogen atom with the hydroxyl radical, $\text{H}-\text{OH}$, hence the radical OH is univalent. Sodium in caustic soda, $\text{Na}-\text{OH}$, is also univalent. In the compounds NaH and NaCl (common salt) sodium is univalent.

An inspection of the formulae of the common acids :



shows that the valencies of the acid radicals are as shown below, each valency being denoted by a stroke :



Valency is further considered in Chapter XX.

CHAPTER XI

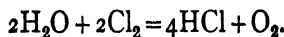
OXYGEN

History.—Oxygen was first isolated by Scheele in 1772 (p. 30), and was discovered independently by Priestley in 1774 (p. 30). Its elementary nature was recognised by Lavoisier (p. 32).

Occurrence.—Oxygen occurs in the free state as a gas of the molecular formula O_2 , to the extent of 21 per cent. by volume or 23 per cent. by weight in the atmosphere, and takes part in processes of combustion; its biological functions in respiration make it important. The gas is sparingly soluble in water, but the small quantity dissolved is essential to the life of fish.

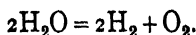
Combined oxygen occurs in water, in vegetable and animal tissues, in nearly all rocks and in many minerals: it occurs to a larger extent (about 50 per cent.) in the earth's crust than any other element.

Preparation of oxygen from water.—Oxygen is obtained from water by passing a mixture of steam and chlorine through a strongly heated silica tube containing pieces of broken porcelain:



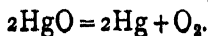
The hydrogen chloride is removed by a wash-bottle containing sodium hydroxide solution and the oxygen may be collected over water.

Oxygen is evolved at the positive electrode in the electrolysis of acidulated water (p. 38):

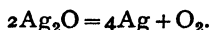


A solution of barium hydroxide with nickel electrodes may also be used, but on prolonged electrolysis an explosive mixture of oxygen and hydrogen may be evolved at the positive electrode.

Preparation of oxygen from oxides.—Oxygen may be obtained by heating certain metallic oxides, viz. those of mercury, silver, gold and platinum. Mercuric oxide heated in a hard glass tube decomposes; globules of mercury collect in the cooler parts of the tube and oxygen gas is evolved and may be collected over mercury:

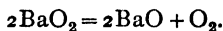


Silver oxide is decomposed at a lower temperature than mercuric oxide :



Higher oxides of metals decompose on heating into oxygen and lower oxides :

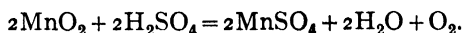
Barium peroxide decomposes into oxygen and barium monoxide (baryta) :



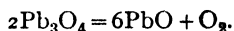
Black **manganese dioxide** decomposes at a *bright-red* heat, giving off oxygen and leaving a brownish-red lower oxide, **trimanganic tetroxide** Mn_3O_4 :



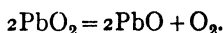
Manganese dioxide evolves oxygen more readily when heated with concentrated sulphuric acid :



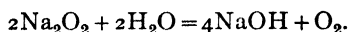
Red lead, which is a higher oxide of lead with the formula Pb_3O_4 , on heating evolves oxygen and leaves a yellow lower oxide of lead called *litharge* or *massicot*, with the formula PbO :



Lead dioxide PbO_2 , a plum-coloured powder, evolves oxygen on heating and leaves lead monoxide, PbO :



Oxygen is evolved by dropping water on **sodium peroxide** Na_2O_2 , but this experiment may result in an explosion :

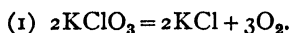


Preparation of oxygen from salts.—Some salts containing oxygen evolve oxygen gas on heating.

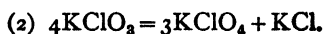
Nitre or saltpetre is **potassium nitrate** KNO_3 . On heating it melts and at a rather high temperature gives off bubbles of oxygen, leaving **potassium nitrite** KNO_2 , which solidifies on cooling :



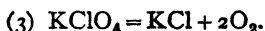
Potassium chlorate crystals when heated in a hard glass tube melt and then evolve oxygen :



As the reaction proceeds, the evolution of gas slackens and the salt becomes pasty, finally almost solid, and at this stage the residue contains potassium chloride and **potassium perchlorate** KClO_4 :



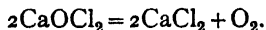
If the temperature is raised the mass fuses again, oxygen is evolved and finally solid potassium chloride remains :



Reactions (1) and (2) proceed *independently* from the commencement. Equations showing the simultaneous formation of oxygen, chloride and perchlorate in a definite ratio are regarded as inaccurate.*

The oxygen obtained from chlorate may contain a little chlorine, which is removed by washing with sodium hydroxide solution.

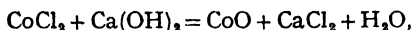
A solution or paste of **bleaching powder** CaOCl_2 heated with a few drops of cobalt chloride solution rapidly evolves oxygen:



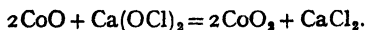
The bleaching powder is decomposed by water into calcium chloride and calcium hypochlorite :



Cobaltous oxide is precipitated by the free lime always contained in the bleaching powder :



but is at once converted by the oxidising action of the hypochlorite into a black peroxide CoO_2 :



This peroxide CoO_2 (or possibly Co_4O_7 or CoO_3) then acts as a catalyst (p. 110) in promoting the decomposition of the calcium hypochlorite.

Potassium permanganate KMnO_4 , which forms purple (almost black) crystals, on heating at 240° evolves pure oxygen without fusing, the crystals falling to a black powder of a mixture of potassium manganate K_2MnO_4 and manganese dioxide :



If the cooled black residue is thrown into a large beaker of water, the potassium manganate dissolves to a *green* solution which almost immediately becomes *pink* from the conversion of the manganate into permanganate by the action of the carbon dioxide dissolved in the water. By adding a little sodium hydroxide (which combines with the carbon dioxide) to the water before the experiment, the green colour remains but becomes pink on adding dilute sulphuric acid.

Chromium trioxide CrO_3 , which forms red crystals, melts on heating and at about 420° evolves oxygen, leaving a green residue of chromic oxide :



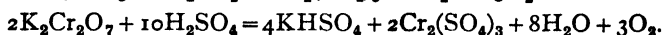
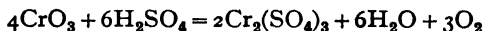
A little of the chromium trioxide sublimes.

* See the papers by Sodeau, *J. Chem. Soc.*, 1902, 81, 1066; and Scobai, *Z. physikal. Chem.*, 1903, 44, 319.

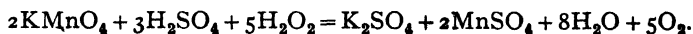
Potassium dichromate $K_2Cr_2O_7$, which forms bright-red crystals, fuses on heating and when *strongly* heated evolves oxygen, leaving a mixture of yellow potassium chromate K_2CrO_4 , soluble in water, and green chromic oxide Cr_2O_3 , insoluble in water :



Chromic acid and potassium dichromate evolve oxygen when heated with concentrated sulphuric acid, chromic sulphate being formed : *

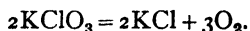


Potassium permanganate explodes violently when heated with concentrated sulphuric acid, but when **hydrogen peroxide** solution is mixed with a solution of the permanganate and **diluted** sulphuric acid, the two compounds mutually decompose each other yielding a nearly colourless solution, and oxygen is evolved :



A solution of 5 gm. of $KMnO_4$ in a cooled mixture of 100 c.c. of water and 50 c.c. of concentrated sulphuric acid is dropped from a tap-funnel into 100 c.c. of 20-volumes hydrogen peroxide in a flask. The oxygen evolved is collected over water.

Laboratory preparation of oxygen.—Potassium chlorate decomposes at a much lower temperature if previously mixed with manganese dioxide. Only the chlorate is decomposed, and in this case no perchlorate is formed :



This reaction is generally used in the laboratory for the preparation of oxygen.†

A mixture of 25 gm. of potassium chlorate with 5 gm. of manganese dioxide (**oxygen mixture**) evolves oxygen freely when heated in a glass tube at a temperature below the melting point of the chlorate. The heating must be carefully regulated, as the decomposition of potassium chlorate, unlike that of mercuric oxide, *evolves* heat and under certain conditions may become explosive.

* The residue from potassium dichromate and sulphuric acid is practically insoluble in water.

† The student should remember that only some of the reactions of preparation of substances are normally used ; *pure* oxygen is best prepared by heating potassium permanganate or by the interaction of acidified permanganate and hydrogen peroxide. Oxygen may be *dried* by means of calcium chloride, concentrated sulphuric acid or phosphorus pentoxide, and must then be collected over mercury.

The mixture is heated in a large test-tube clamped in a horizontal position and fitted with a fairly wide glass delivery tube passing through a cork in the test-tube and dipping at the other end beneath the water in a pneumatic trough. Over this end is supported a glass cylinder full of water and standing on a beehive shelf in the trough (Fig. 61). The

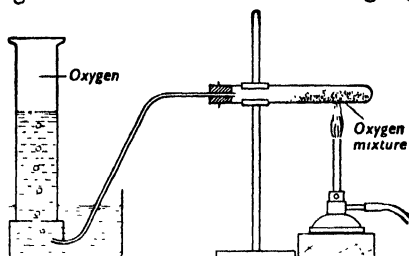


FIG. 61.—Preparation of oxygen.

mixture is cautiously heated with a small flame, beginning at the end near the cork, and the flame is withdrawn from time to time when the evolution of gas begins to be violent. The delivery tube must be taken out of the water before the test-tube is allowed to cool, since otherwise water will be forced back into the hot tube and crack it.

Warning.—Manganese dioxide adulterated with powdered coal or antimony sulphide explodes violently on heating with chlorate. Serious and even fatal accidents have been caused in this way, and a *little* of the mixture should always be heated in an open test-tube before beginning the experiment in order to be sure that no deflagration occurs.

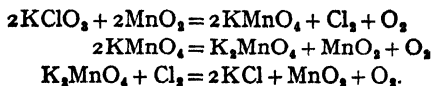
Catalysis.—The manganese dioxide in the oxygen mixture undergoes no *permanent chemical* change in the reaction and may be recovered by dissolving out the potassium chloride from the residue with water. Other oxides such as ferric oxide and cupric oxide act similarly to manganese dioxide and are also left chemically unchanged after the reaction.

This action was discovered by Döbereiner in 1820, and is an example of what was called **contact action** by Mitscherlich in 1833 and **catalysis** by Berzelius in 1835.

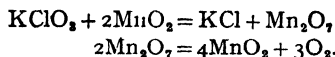
A catalyst is a substance which accelerates a chemical reaction without itself undergoing any permanent chemical change.

If several products are obtainable in a reaction, a catalyst may be able to direct the course of the reaction (p. 419).

The catalytic action of manganese dioxide was explained by McLeod (1889) as due to a cycle of reactions :



Fowler and Grant (1890) suppose that a higher oxide of manganese is alternately formed and reduced :



If a *small* quantity of finely powdered MnO_2 (Mn_2O_7 is better) is added to chlorate just fused in a test-tube there is a vigorous evolution of oxygen and the material becomes pink.

Many catalytic actions can be explained by such "intermediate compound" or "cyclic action" theories.

Many other examples of catalytic action will be considered later (see Index under "Catalysis"); it should be remembered that the action may vary in different cases and that no *general* explanation of catalysis is likely to be correct.*

Physical properties of oxygen.—Oxygen is a colourless gas, without smell or taste. It is slightly heavier than air.

Oxygen is only slightly soluble in water, but the small amount of oxygen dissolved in natural waters is sufficient for the respiration of fish. Oxygen is difficult to liquefy: the liquid is pale blue in colour and is appreciably magnetic. At still lower temperatures light blue solid oxygen is obtained. It should be noted that solid oxygen cannot be obtained by the rapid evaporation of the liquid (as can solid nitrogen); the liquid must be cooled in liquid hydrogen.

Combustion.—The combination of substances with oxygen, when attended with the evolution of heat and light, is called combustion. Substances which burn in air do so with much greater brilliancy in pure oxygen, since the nitrogen in air acts as a diluent, absorbing part of the heat given off in the combustion. Some substances, such as phosphorus, oxidise *slowly* when exposed to air without catching fire, because the heat produced by oxidation is dissipated too rapidly to raise the temperature to the *ignition point*.

Finely divided phosphorus, obtained by the evaporation of a solution of phosphorus in carbon disulphide poured on filter paper, takes fire spontaneously in air.

Finely divided lead, called pyrophoric lead (made by heating lead tartrate), catches fire and glows when a tube containing it is cut open and the powder shaken out into the air: fumes of lead oxide are formed.

Combustion of non-metals in oxygen.—Some non-metallic elements, such as phosphorus, sulphur, and carbon, burn in oxygen to form *acidic oxides*, *i.e.* oxides which form acids on solution in water (see p. 42).

* See McLeod, *J. Chem. Soc.*, 1889, 55, 184; Fowler and Grant, *ibid.*, 1890, 57, 272; E. Jobling, *Catalysis and its Industrial Applications*, 2nd ed., 1920; S. K. Tweedy, *J. Soc. Chem. Ind.*, 1926, 45, 157, 177. Many statements about catalysis found in elementary works are either incorrect or out of date.

Hydrogen on combustion forms water, which is a *neutral oxide*, i.e. has no acidic or basic reaction.

The combustion of solids such as phosphorus, sulphur and carbon in oxygen may be demonstrated by the following experiments. The

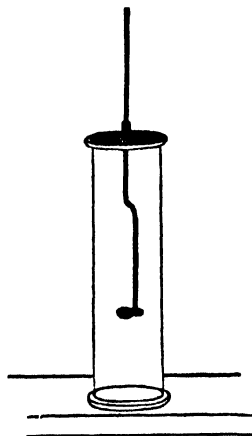
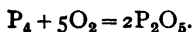


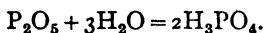
FIG. 62.—Gas jar and deflagrating spoon.

substances contained in the bowls of *deflagrating spoons* are kindled and placed in jars of oxygen (Fig. 62).

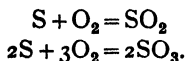
(1) White phosphorus is cut under water, a small piece rapidly dried by pressing between filter papers, and put in the spoon with dry crucible tongs. *The dry phosphorus must on no account be handled with the fingers* as it may take fire. The phosphorus is kindled by touching it with a hot wire and put into the jar, when it burns in the oxygen with an exceedingly brilliant white flame, producing a dense white cloud of phosphorus pentoxide which settles in flocks on the sides of the dry jar :



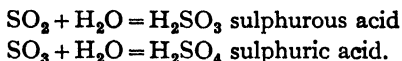
When water is poured into the jar the oxide dissolves and phosphoric acid H_3PO_4 is formed, which changes the colour of blue litmus solution to red :



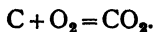
(2) A piece of roll sulphur when kindled in a spoon burns with a bright blue flame when introduced into a jar of oxygen. The gas sulphur dioxide SO_2 is the main product of the combustion, but a little solid sulphur trioxide SO_3 is also formed, which renders the gas slightly cloudy :



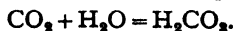
When shaken with water, the products of combustion dissolve, yielding a solution which reddens litmus :



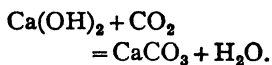
(3) A piece of wood charcoal strongly heated in a spoon burns brightly, often throwing off bright sparks, when placed in oxygen. Carbon dioxide CO_2 is the chief product of the reaction, although a little carbon monoxide CO is generally formed (p. 417) :



When the gas is shaken with water, a little carbon dioxide dissolves forming a solution of the very weak and unstable carbonic acid H_2CO_3 , which changes the blue colour of litmus to a port-wine red colour :



If another jar of carbon dioxide is prepared and the gas is shaken with lime water, this becomes milky from the formation of a precipitate of calcium carbonate CaCO_3 :



(4) A jet of hydrogen gas, prepared by the action of dilute sulphuric acid on zinc (see p. 129), burns in a jar of dry oxygen, producing water (Fig. 63) which condenses as a dew on the cold sides of the jar :

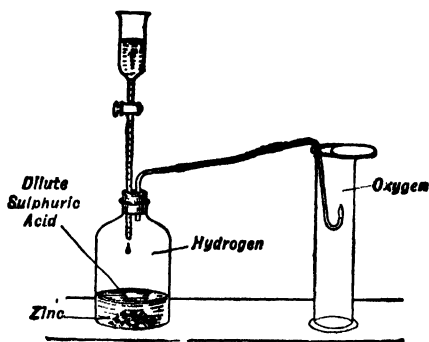
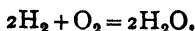


FIG. 63.—Hydrogen burning in oxygen.



If a jet of oxygen is thrust into an inverted jar of hydrogen burning at the mouth, the oxygen takes fire and continues to burn in the atmosphere of hydrogen (Fig. 64). The terms **combustible** and **supporter of combustion** are therefore purely relative (see p. 411).

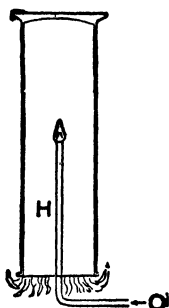


FIG. 64.—Oxygen burning in hydrogen.

Compressed oxygen gas (prepared from the air, p. 119, and sold in steel cylinders) is used for the oxy-hydrogen blowpipe. When oxygen and hydrogen (or coal gas, or acetylene, p. 403) are supplied separately to a blowpipe jet consisting (Fig. 65) of two concentric tubes, the oxygen being inside, a blue, pointed, intensely hot flame is produced in which even platinum wire melts. The oxy-coal gas and oxy-acetylene

blowpipes are used in welding or cutting iron or steel.

Combustion of metals in oxygen.—Some metals, when strongly heated, burn in oxygen to form oxides. These oxides are nearly always **basic oxides**, *i.e.* oxides which form salts with acids (p. 42). Other metals

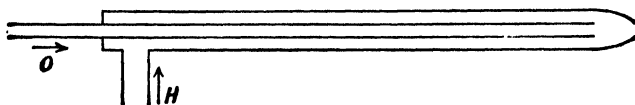
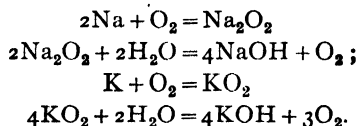


FIG. 65.—Oxy-hydrogen blowpipe (section).
Hydrogen enters through H and oxygen through O.

(such as copper and lead) do not burn in oxygen, but combine with it on heating to form oxides.

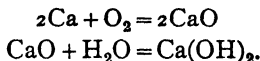
(1) Sodium and potassium, when heated in iron deflagrating spoons until they begin to burn and then lowered into *dry* jars of oxygen, burn with bright yellow and lilac flames, respectively, forming orange-yellow solid *peroxides* (p. 43) which, *when cold*, may be dissolved in water with evolution of oxygen and formation of alkaline solutions which turn red litmus blue and contain sodium and potassium hydroxides :



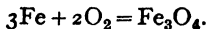
(Note that the formulae of sodium and potassium peroxides are different, and that the basic oxides Na_2O and K_2O are *not* formed in these experiments, where the oxygen is in excess.)

(2) Magnesium ribbon held in crucible tongs, ignited in air and inserted into a jar of oxygen, burns with a blinding white light, forming white solid magnesium oxide MgO , which is a sparingly soluble basic oxide and turns moist red litmus paper blue.

(3) A piece of calcium when strongly heated in an iron deflagrating spoon burns brightly in oxygen, forming calcium oxide CaO , which turns moist red litmus blue :



(4) A spiral of iron wire tipped with a bit of burning wood, burns brilliantly, giving off bright sparks, when lowered into a bottle of oxygen (Fig. 66). Ferrosoferric oxide Fe_3O_4 is formed in fused globules, which fall on a layer of sand. It has no action on litmus :



Since ferrosoferric oxide may be regarded as a compound of ferrous oxide and ferric oxide, $\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$, it is sometimes called a **mixed oxide**.

Heat of combustion.—By the combustion of substances in oxygen large amounts of heat are given out. In everyday life we make use of the combustion of coal or gas in air (containing free oxygen) as a source of heat. Chemical reactions accompanied by the *evolution of heat* are called **exothermic reactions**.

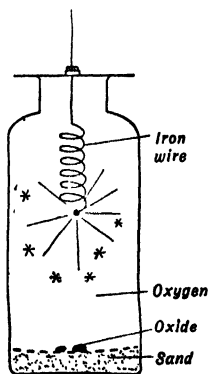
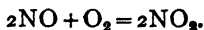


FIG. 66.—Iron wire burning in oxygen.

In the decomposition of mercuric oxide heat must be supplied, and the reaction, which is accompanied by the *absorption of heat*, is called an *endothermic reaction*.

Tests for oxygen.—The test for pure oxygen (or a *large* proportion of oxygen mixed with an indifferent gas such as nitrogen) is the rekindling of a glowing chip of wood ; the only gas which also responds to this test and might be mistaken for oxygen is nitrous oxide N_2O . The two are distinguished by the fact that nitrous oxide is much more soluble than oxygen in water, and by the formation of red nitrogen dioxide NO_2 with free oxygen but not with nitrous oxide (unless it contains some free oxygen) :

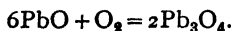


The nitric oxide test will detect free oxygen when present in a mixture which does not respond to the glowing chip test.

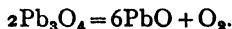
Estimation of oxygen.—Oxygen is absorbed from gaseous mixtures in gas analysis by : (i) a solution of pyrogallol and caustic potash, which turns black ; (ii) phosphorus (this does not glow in pure oxygen) ; (iii) an acid solution of chromous chloride, which turns from blue to green owing to the formation of chromic chloride : $4\text{CrCl}_2 + \text{O}_2 + 4\text{HCl} = 4\text{CrCl}_3 + 2\text{H}_2\text{O}$; (iv) by mixing the gas with excess of hydrogen and sparking in a eudiometer, or adding enough hydrogen to form a non-explosive mixture and passing over platinised asbestos at a dull-red heat (or gently heated palladium), when water is formed ; one-third of the contraction of the gas then represents the oxygen contained in it : $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ (liquid). The last method can be used only in the absence of other gases which react with either oxygen or hydrogen under the conditions of experiment (*e.g.* hydrocarbons or nitrous oxide).

Oxygen from air.—Oxygen may be obtained from the atmosphere, which is a mixture of oxygen and nitrogen (and a little argon), by heating mercury in a confined volume of air, when the oxygen forms mercuric oxide (Lavoisier's experiment, p. 31), and then heating the oxide strongly when pure oxygen is evolved (p. 15). Other substances may be used more conveniently than mercury.

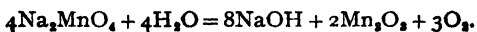
If yellow lead monoxide or massicot PbO is *carefully* heated in an iron dish and freely exposed to air, it takes up oxygen and forms red lead, the atmospheric nitrogen being unabsorbed :



Red lead on heating more strongly decomposes into massicot and oxygen :



When steam is passed over sodium manganate heated to dull redness in a copper tube, oxygen is evolved :

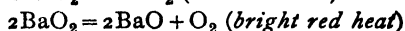
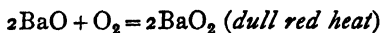


By passing air over the heated mixture oxygen is taken up and sodium manganate is formed, the nitrogen passing on :

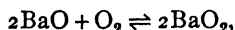


The manganate may now be decomposed by steam, when the oxygen taken up from the air is liberated and the processes may be repeated.

Barium monoxide or baryta BaO takes up oxygen from air when heated to *dull redness*, forming barium peroxide BaO_2 . The nitrogen is left unabsorbed. The peroxide on heating to *bright redness* evolves pure oxygen, leaving barium monoxide. The two reactions :



can both take place under suitable conditions, and each reaction may be said to be reversible. This is expressed by writing the equation in the form :



the arrows showing that it may take place in either direction.

These reactions were the basis of the now obsolete Brin process. In this two different pressures were used instead of two different temperatures.

Barium peroxide heated in a closed vessel at a constant temperature decomposes into baryta and oxygen. The oxygen molecules by collision with the baryta form barium peroxide again. The higher the pressure of the oxygen the more frequent are the collisions and the greater is the rate of recombination. The rate at which barium peroxide molecules break up is constant at a given temperature, hence at a certain pressure of oxygen the rate at which peroxide forms becomes equal to the rate at which it decomposes. A state of equilibrium is set up at a definite pressure of oxygen. If the pressure of the oxygen is raised the collisions become more frequent, more combination takes place, and if the pressure is *maintained* above the equilibrium pressure, oxygen is reabsorbed by the baryta. If the pressure of the oxygen is decreased, more peroxide decomposes, since less oxygen returns to it by collisions, and if gas is *continuously* pumped off *all* the peroxide is ultimately decomposed.

Baryta was heated to dull redness in purified air in iron retorts under pressure, when it absorbed oxygen forming barium peroxide. The atmospheric nitrogen was removed by a pump and the pressure reduced, when the peroxide decomposed evolving pure oxygen.

All the oxygen made technically from the atmosphere is now produced by a physical process, viz. the fractional distillation of liquid air.

Liquefaction of gases.—Ammonia gas was liquefied by compression by Van Marum and in 1799 by cooling by Guyton de Morveau.

Sulphur dioxide was liquefied by cooling by Monge and Clouet; in 1806 chlorine was reduced to the liquid state by Northmore. In 1823 liquid chlorine was again obtained by Faraday by warming chlorine hydrate in one limb of a sealed Λ -tube (Fig. 67), the other limb of which was cooled in a freezing mixture; when the pressure reached the vapour pressure of the liquid at this temperature the chlorine liquefied. In later experiments Faraday liquefied hydrogen sulphide, hydrogen chloride, carbon dioxide, nitrous oxide, cyanogen and ammonia; but oxygen, nitrogen and hydrogen resisted all attempts to reduce them to liquids.

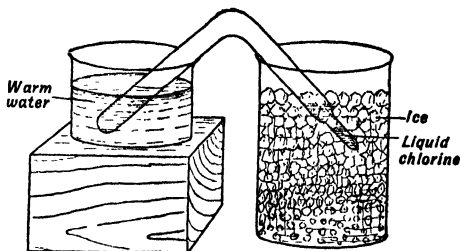


FIG. 67.—Liquefaction of chlorine.

In 1869 Andrews discovered that a gas cannot be liquefied by any pressure, however high, unless it is previously cooled below what is called the critical temperature of the gas. The critical temperature of oxygen is -119° .

The critical temperatures of the so-called permanent gases lie below the lowest temperatures attained by older experimenters. As soon as it was clear that strong cooling was necessary and that high pressures alone could never succeed in the case of these gases, the problem was solved.

The cooling process used in the modern liquefaction apparatus depends on the Joule-Kelvin effect, and is quite different from the cooling produced by adiabatic expansion. In adiabatic expansion a compressed gas is allowed to expand suddenly and do external work against the atmospheric pressure. The energy equivalent of this work is taken from the gas, which is therefore cooled. In the Joule-Kelvin effect, which is produced in so-called "free expansion", the work of expansion is internal and is done in separating the molecules against their attractive forces.

A given mass of gas of volume v_1 (Fig. 68) is forced under a pressure p_1 through a nozzle into a space under a lower pressure p_2 (say $\frac{1}{2}p_1$), when it occupies a larger volume v_2 .

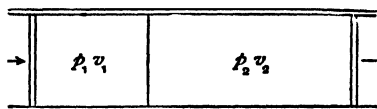


FIG. 68.—Diagram illustrating free expansion of a gas.

The work done on the gas is $p_1 v_1$, that done by the gas is $p_2 v_2$. If the gas obeyed Boyle's law, as is approximately the case, $p_1 v_1 = p_2 v_2$ ($v_2 = 2v_1$; $p_1 = 2p_2$) and no external work would be

done; if no other effect were involved there would be no change of temperature. Since, however, v_2 is greater than v_1 the molecules of the gas will have separated, and if there is a slight attraction between them, *internal* work will have been spent in separating them. The energy required for this *internal* work is taken from the heat of the gas and a slight cooling effect results. If air at 0°C . and under a pressure of 100 atm. is expanded through a valve to atmospheric pressure, the fall of temperature will be about 25°F .

Liquid air.—The apparatus for the liquefaction of air is shown diagrammatically in Fig. 69. Air is drawn through purifiers to remove carbon

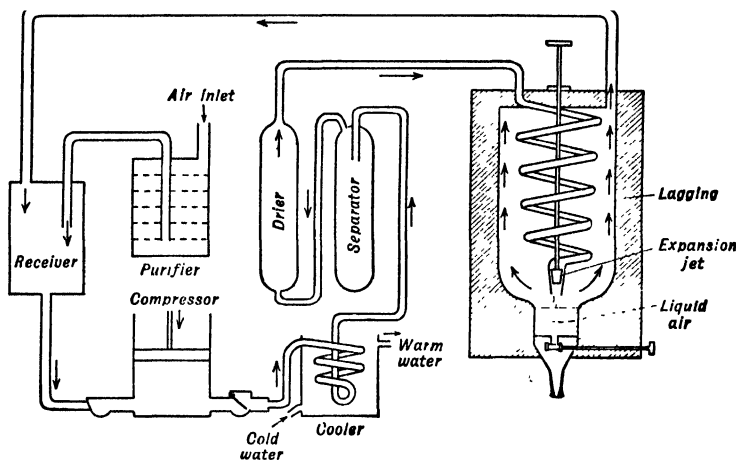


FIG. 69.—Air liquefaction apparatus.

dioxide and then compressed. The heat of compression is taken out by a cooler and the air passes through an apparatus in which moisture is removed. The compressed air then expands through a jet and in so doing becomes cooled. The cold air sweeps over the outside of a spiral metal pipe bringing the compressed air to the jet, and so cools the compressed air before expansion. This cooling effect accumulates and finally the air becomes so cold that it liquefies on leaving the jet. Liquid air as obtained from the liquefier is richer in oxygen than gaseous air. Usually it contains from 50 to 60 per cent. by weight of oxygen as compared with 23 in gaseous air.

The liquid air is a mixture of liquid nitrogen (boiling point -196°) and liquid oxygen (boiling point -183°). The nitrogen is more volatile and tends to boil off first in evaporation, although some oxygen evaporates with it (see p. 5). The separation of the two gases is brought about by letting the evolved gas bubble through liquid air rich in oxygen in a tall rectifying column. The oxygen in the gas condenses and nearly

pure nitrogen gas passes off, leaving nearly pure liquid oxygen which is then evaporated.

In the Claude process the compressed air is used to work an expansion engine, when the heat equivalent of the work done is extracted from the air ; in this way it can be cooled through 75° .

Liquid air or oxygen is stored in small amounts in Dewar ("thermos") vessels with an annular vacuum jacket, silvered to reflect heat, or in large amounts in spherical metallic vacuum vessels, holding 5 to 30 galls., the inner vessel being suspended by a thin metallic neck and the annular space exhausted. A high vacuum is produced by means of a tube of absorbent charcoal open at the end exposed to the vacuum space, and with the other (closed) end immersed in the liquid itself.

Industrial preparation of oxygen from air.—At first sight it would seem possible to obtain oxygen from liquid air by allowing the more volatile nitrogen to boil off leaving the liquid oxygen. The boiling points are too close to allow of this and the figures in the table (from Linde's experiments) show that such a process would be attended by great loss and could never give oxygen sufficiently pure for industrial use. (Weight percentages are shown.)

% liquid not evaporated	% O_2 in liquid	% O_2 in gas evaporating	% original O_2 left in liquid
100	23	7.5	100
50	37.5	15	80
30	50	23	65
20	60	34	52
10	77	52	33
5	88	70	19

The actual process introduced by Linde in 1902 makes use of *fractional distillation* by means of a rectifying column in which the escaping gas is scrubbed by liquid passing in the other direction. Claude in 1906 introduced the principle of liquefying the air in stages, obtaining two liquids, one rich in oxygen and the other in nitrogen, which are poured into the rectifying column at the appropriate places. The column shown in Fig. 70 is used in the Claude processes.

Compressed air which has been cooled by expansion in an engine enters at *A*, when it partly liquefies and enters a vessel containing two sets of vertical tubes *B*. Liquid richer in oxygen drains into *A* while gas richer in nitrogen rises and passes through the outer ring of tubes. Both sets of tubes are cooled in liquid oxygen in *S*. The part liquefied in the outer ring is richer in nitrogen (as the gas is under increased pressure it liquefies at the temperature of the liquid oxygen) and the liquid rich in nitrogen collects in the annulus *C*. This nitrogen-rich liquid is sent to the top of

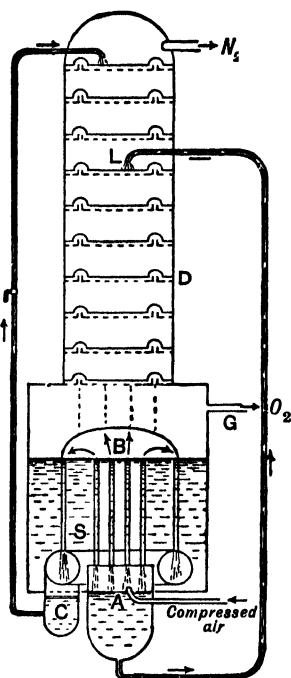


FIG. 70.—Liquid air fractionating column.

the upper rectifying column, where the nitrogen tends to boil off. Into this column the oxygen-rich liquid from *A* is discharged at *L*. The liquid running down the column *D* meets gas rich in oxygen rising from *S*. The liquid loses its more volatile constituent nitrogen as gas, whilst the gas rising is robbed of its less volatile constituent oxygen by the liquid, the heat of condensation of the oxygen serving to evaporate the nitrogen. Finally, nitrogen gas escapes at the top of the column and liquid oxygen drops into *S* where it evaporates, the gas passing through heat interchangers to compressors, which pump it into steel cylinders for sale. In practice it is not economical to make both pure oxygen and pure nitrogen with the same apparatus; when oxygen is made a nitrogen-rich gas is waste and when nitrogen is made an oxygen-rich gas is waste. Sometimes another fractionating column below the apparatus is used.

Oxygen gas is used in blowpipes with hydrogen, coal gas and acetylene for welding and cutting metals. It is used in some industrial processes and medicinally in cases of pneumonia and gas poisoning, and mixed with nitrous oxide, ether vapour or other

anaesthetic. Some carbon dioxide is often mixed with the oxygen, as this stimulates breathing, and carbon dioxide is also used in cases of poisoning and collapse for restoring respiration. Liquid oxygen mixed with powdered charcoal has been used as an explosive.

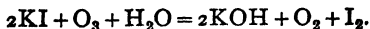
OZONE

History.—Van Marum in 1785 noticed that oxygen gas through which an electrical discharge has passed acquires a peculiar smell and tarnishes mercury. This smell is easily noticed in a physics laboratory when experiments on electrostatics are in progress. Cruickshank in 1800 observed the same smell in electrolytic oxygen, but the fact that the odour is due to a peculiar gas was first recognised in 1840 by Schönbein, who gave the substance the name *ozone* (Greek, *ozo*, I smell). He found that it is also produced by the slow oxidation of phosphorus in moist air, and that it is a powerful oxidising agent, liberating iodine from potassium iodide solution.

Occurrence.—The invigorating properties of sea air are popularly attributed to "ozone" and this is produced by electric discharges in the atmosphere and especially by the action of ultra-violet light from the sun

on the oxygen in the upper layers of the atmosphere. According to Paneth (1938) London air contains one millionth of a per cent. by volume of ozone.

Preparation of ozone.—A few sticks of freshly scraped phosphorus are placed in a stoppered bottle with a little water. When the fumes have subsided, a piece of paper dipped into a solution of potassium iodide and starch ("starch-iodide paper") introduced into the bottle is turned blue from liberation of iodine:



It is difficult to obtain pure ozone, which is very explosive, but a mixture of ozone with oxygen or with air is easily made by the action of a "silent electric discharge" on these gases. The best apparatus for the experiment is **Brodie's ozoniser** (Fig. 71).

The oxygen or air is passed slowly through the annular space between two glass tubes, the inner filled with dilute sulphuric acid or copper sulphate solution, and the whole apparatus placed in a jar of the liquid. The wires from a coil dip into the two liquids, which form electrodes and at the same time serve to cool the apparatus. The gas is conducted away through glass tubes with ground-glass joints, or joints of ordinary corks. Rubber is very quickly destroyed by ozone.

Siemens' ozoniser (Fig. 72) consists of two concentric glass tubes, the outer covered and the inner lined with tinfoil to form the electrodes.

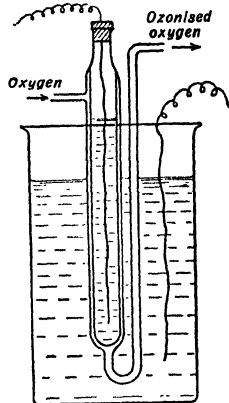


FIG. 71.—Brodie's ozoniser.

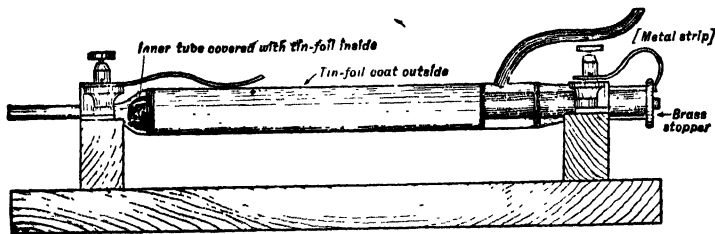
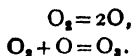


FIG. 72.—Siemens' ozoniser.

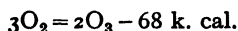
The formation of ozone in the apparatus is shown by the smell of the issuing gas, which may contain about 5 per cent. of it by volume.

The formation of ozone in the ozoniser probably depends on the dissociation of oxygen molecules into atoms by the silent discharge (or other agent), an oxygen atom then combining with an oxygen molecule to form ozone:



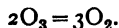
Ozone is formed by the action of ultra-violet light on oxygen; it is present in the oxygen evolved in the electrolysis of dilute sulphuric acid (sp. gr. 1.1), and is produced in some chemical reactions, *e.g.* by the action of concentrated sulphuric acid on barium peroxide and by heating periodic acid; ozone is also present in the air round hydrogen and hydrocarbon flames.

When ozonised oxygen is passed through a tube cooled in liquid air a cornflower-blue liquid separates; this is a solution of ozone in liquid oxygen. By strong cooling and evaporating under low pressure black crystals of pure solid ozone are produced, which on raising the temperature melt and then evaporate to a dark-blue gas which is pure ozone. The density corresponds with the formula O_3 . Pure ozone is very explosive, since it is strongly endothermic with respect to oxygen (O_2) (see p. 115):

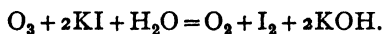


Properties of ozone.—The properties of ozone to be described mostly refer to a mixture of ozone with oxygen or air.

Ozone is more soluble than oxygen in water. It is decomposed by heat and when the gas coming from an ozoniser is passed through a heated glass tube all the ozone is converted into oxygen:



Ozone is a powerful oxidising agent and liberates iodine from a solution of potassium iodide:



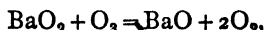
In this reaction the volume of the gas remains unchanged, since one atom of oxygen in the ozone molecule oxidises the iodide and the other two atoms form a molecule of ordinary oxygen.

Chlorine, bromine, hydrogen peroxide and nitrogen peroxide also liberate iodine from potassium iodide; they are distinguished from ozone by the tests described on p. 126.

Ozone produces a remarkable effect on mercury: when ozonised oxygen is passed into a clean dry flask containing a little mercury, the meniscus is destroyed and the metal adheres to the glass. On shaking with water, the mercury recovers its original form. According to H. B. Baker this action is due to oxidation to Hg_2O which dissolves in mercury.

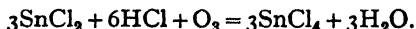
Ozone is catalytically decomposed in contact with metallic silver and platinum, and with manganese dioxide, lead dioxide and silver oxide.

Barium and hydrogen peroxides react with ozone:

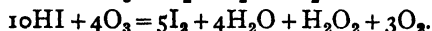


but the gas has no action on chromic acid or potassium permanganate. Sulphur dioxide is oxidised to the trioxide: $3SO_2 + O_3 = 3SO_3$. This

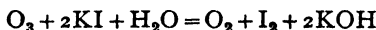
is one of the few reactions in which the ozone molecule oxidises as a whole ; another is with stannous chloride solution :



Ozone bleaches indigo solution and vegetable colours, and converts moist sulphur, phosphorus, and arsenic into their highest oxy-acids. It liberates halogens from their hydrides :

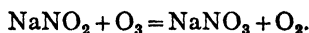


The liberation of iodine from potassium iodide :

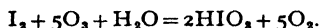


occurs in a neutral solution, which then becomes alkaline. If a piece of neutral litmus paper is moistened with potassium iodide solution and exposed to a gas containing ozone, the wetted portion is turned blue owing to liberation of alkali.

In the determination of ozone, the iodine liberated from a *neutral* solution of potassium iodide may be titrated with sodium thiosulphate after slight acidification. Another method depends on the oxidation of sodium nitrite solution :



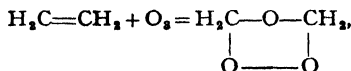
Moist iodine is oxidised by ozone to iodic acid :



Dry iodine is converted into a yellow powder I_4O_9 , without change of volume of the gas : $2\text{I}_2 + 9\text{O}_3 = \text{I}_4\text{O}_9 + 9\text{O}_2$. An alkaline solution of potassium iodide is oxidised to iodate (KIO_3) and periodate (KIO_4).

Ozonised air is used for sterilising drinking water and has also been used in removing unpleasant odours from air in confined spaces, *e.g.* underground railways.

Ozone is also used in oxidising some organic compounds ; it combines with double linkages to form ozonides, which are decomposed by water, *e.g.* ethylene :

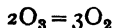


which with water gives formaldehyde $\text{H}_2\text{C}=\text{O}$ and hydrogen peroxide H_2O_2 .

Formula of ozone.—The formula O_3 of ozone was first suggested by Odling in 1861 and was experimentally confirmed in 1866-8 by Soret.* If all the ozone in a given volume of ozonised oxygen is absorbed by oil

* See his papers in "Eau oxygénée et ozone", *Classiques de la Science*, III (A. Colin. Paris).

of turpentine or oil of cinnamon (which absorb ozone *in toto*), and if the ozone in another equal volume of the same ozonised oxygen is decomposed by heat, the equation :



shows that *the contraction on absorption is twice the expansion on heating*.

Soret used two flasks of 250 c.c. capacity inverted over water, the ozone in one being decomposed by heating and that in the other absorbed by turpentine. Newth's apparatus is more convenient. Instead of measuring the expansion when ozone is converted into oxygen on heating, it measures the *contraction* of a given volume of oxygen when ozonised, and then by introducing turpentine into the resulting gas measures the further contraction when the ozone is absorbed by the turpentine.

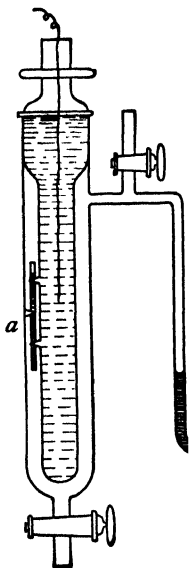


FIG. 73.—Newth's apparatus.

The apparatus (Fig. 73) consists of two concentric tubes, the inner fitted into the outer by a ground-glass joint. The inner tube contains dilute sulphuric acid and the apparatus filled with dry oxygen is supported in a jar of water and crushed ice. Wires from a coil dip into the liquids. By means of projections from the inner and outer tubes a *thin* glass tube containing turpentine is held in position in the annular space. The manometer contains concentrated sulphuric acid * coloured with indigo. The levels are adjusted and the oxygen is ozonised. The contraction after cooling to the original temperature is read off. The tube containing the turpentine is broken by twisting the inner tube and the contraction on absorption (after the gas has cooled again) will be found to be twice the contraction on ozonisation. This experiment when carefully performed gives excellent results.

Soret in his second research used Graham's law of diffusion. If ozone has the formula O_3 (density 24) it should diffuse rather more slowly than carbon dioxide (density 22) but more rapidly than chlorine (density 35.5). The diffusion rates are inversely proportional to the square roots of the densities:†

$$\frac{\text{Rate of diffusion of CO}_2}{\text{Rate of diffusion of O}_3} = \frac{\sqrt{24}}{\sqrt{22}}; \quad \frac{\text{Rate of diffusion of Cl}_2}{\text{Rate of diffusion of O}_3} = \frac{\sqrt{24}}{\sqrt{35.5}}.$$

Soret allowed the gases to diffuse into pure oxygen and measured the relative diffusion v/V of each gas mixed with oxygen, where v is the volume of gas diffusing and V the total volume present in the original

* The acid does not act on ozone; mercury cannot be used (p. 122), and ozone is rather too soluble in water.

† See Partington and Stratton, *Intermediate Chemical Calculations*, p. 28.

mixture. The rate of diffusion of oxygen in both directions was the same; the rates of diffusion of the other gases were (i) proportional to the numbers of molecules present in a given volume (measured by V) and (ii) inversely proportional to the square roots of the densities. The ratios v/V were therefore inversely proportional to the square roots of the densities of the diffusing gases.

The apparatus (Fig. 74) consisted of three glass tubes B' , B and C , placed over sulphuric acid in E and separated by sliding glass plates with holes, so that the tubes could be put in communication or separated. B' was filled with pure oxygen. B was first full of acid and the mixture of one of the gases with oxygen, prepared in C , was transferred to B by sliding the glass partition o . The glass plates between B and B' had perforations which could be brought between the two cylinders by sliding the plate o' . Diffusion from B to B' was allowed to go on for forty-five minutes, when the plate o' was slid back and the cylinders again isolated. The gas in B' could be driven out into a solution of baryta when carbon dioxide was diffused, or potassium iodide for chlorine or ozone. The ratio of the ozone in the original gas and in the gas in B' was determined from the ratio of the amounts of iodine liberated by the gases. If u u' are the amounts of iodine liberated by the gas in B' and that remaining in B , respectively, then $v/V = u/(u + u')$. The relative rates of diffusion were found to be: chlorine, 0.227; ozone, 0.271; carbon dioxide, 0.290.

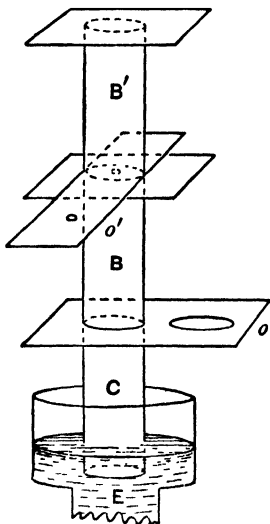


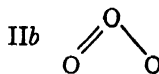
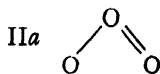
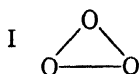
FIG. 74.—Soret's diffusion apparatus.

The ratio of these values for ozone and chlorine is $227/271 = 0.838$. The inverse ratio of the square roots of the densities, assuming that ozone is O_3 , is $\sqrt{24/35.5} = 0.822$. The diffusion ratio for carbon dioxide and ozone is $271/290 = 0.93$, whilst the inverse ratio of the square roots of the densities, again assuming O_3 , is $\sqrt{22/24} = 0.95$. The agreement is to 3 per cent., which is satisfactory as the ozonised oxygen contained only 5 per cent. of ozone by volume.

Ladenburg in 1898 obtained nearly pure ozone by the evaporation of the liquid and compared the times of effusion of equal volumes of this gas and of oxygen in a Bunsen's effusion apparatus; he found a density of 22, in satisfactory agreement with the formula O_3 , and the density 24 was found in 1922 with pure ozone in a Dumas' apparatus by Riesenfeld and Schwab.

The ozone molecule is triangular in shape with the angle at the top about 117° . It was at one time supposed that the three oxygen atoms were

linked together as shown in I, but for various reasons it is now thought that the bottom linkage is taken up into one side or the other to form a double bond and the actual state of the molecule is a resonance hybrid of the two forms IIa and IIb (see p. 264B) :



Tests for ozone.—The difficulty of detecting ozone when there is not enough to show its characteristic smell (1 volume in 500,000) is that chlorine, bromine, hydrogen peroxide vapour and some oxides of nitrogen ($\text{N}_2\text{O}_3, \text{NO}_2, \text{N}_2\text{O}_4$) also liberate iodine from potassium iodide.

Test papers prepared by soaking filter paper with alcoholic solutions of the reagents below react as stated ; they are unaffected by hydrogen peroxide :

		<i>Ozone</i>	<i>Halogens</i>	<i>Oxides of nitrogen</i>
Tetramethyl-base	-	violet	blue	straw-yellow
Benzidine	- -	brown	blue, then red	blue

Hydrogen peroxide vapour and oxides of nitrogen may be removed by passing the gas through a solution of chromic acid.

Hydrogen peroxide and ozone are destroyed by passing the gas through manganese dioxide, whilst oxides of nitrogen pass on and will decolorise dilute permanganate solution. The latter will absorb oxides of nitrogen and hydrogen peroxide and allow ozone to pass. Hydrogen peroxide is then detected by bubbling the gas through a solution of potassium ferricyanide and ferric chloride, which is turned blue.

CHAPTER XII

HYDROGEN

History.—Hydrogen gas was first prepared by Boyle from steel filings and hydrochloric acid, and from iron nails and dilute sulphuric acid (p. 25), although Van Helmont (1648) had described an inflammable gas (*gas pingue*). It was carefully investigated by Cavendish in 1766 and called by him *inflammable air*.

Occurrence.—Free hydrogen is said to occur in small quantities in some volcanic gases, it is found in most specimens of meteoric iron, and the outer atmosphere of the sun is found by the spectroscope to consist mostly of hydrogen.

Hydrogen in combination is more common. With oxygen it forms water H_2O ; with sulphur hydrogen sulphide H_2S ; with carbon a large number of compounds called hydrocarbons, which make up petroleum. All organic substances of vegetable and animal tissues contain hydrogen, and this element is an essential constituent of acids and alkalis. The *artificial* products coal gas and water gas contain free hydrogen.

Preparation.—Hydrogen may be obtained in a large number of different ways *only a few of which are convenient for the laboratory preparation*; some are used in industry and not in the laboratory. These methods may be classified as follows:

1. From *water*:
 - (a) by *electrolysis*;
 - (b) by the action of *metals*;
 - (c) by the action of *carbon*.
2. From *acids* by the action of *metals*.
3. From *alkalis* by the action of *metals*.
4. Miscellaneous industrial processes.

Hydrogen from water. The different methods are:

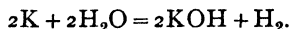
(1) *By electrolysis.* The use of the water voltameter has been explained in Chapter IV. Water acidulated with dilute sulphuric acid is commonly used, but a dilute solution of sodium or barium hydroxide may also be

used. If the anode consists of a pool of zinc amalgam in acidulated water, the oxygen liberated combines with the zinc and only hydrogen is evolved from the cathode (*Bunsen's voltameter*). On the large scale sodium hydroxide solution with iron (or nickel-plated iron) electrodes is used.

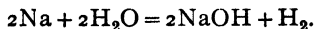
Pure hydrogen is best prepared by the electrolysis with nickel electrodes of warm saturated barium hydroxide solution. The gas is passed over hot platinum gauze (not platinised asbestos, which forms a trace of silicon hydride) to burn any oxygen in it, then dried by caustic potash (*not* concentrated sulphuric acid, which gives off a little sulphur dioxide by reduction) and pure redistilled phosphorus pentoxide. The gas may then contain a little nitrogen (from air leaks). It is passed into an exhausted bulb containing metallic palladium, which is gently heated. Only the hydrogen is absorbed by the palladium. The nitrogen is pumped out and on strongly heating the bulb, pure hydrogen is evolved.

(2) *By the action of metals.* The metals lithium, sodium, potassium and calcium act on water at the ordinary temperature, the first three violently but calcium only slowly unless the water is hot, when the action is more vigorous.

The heat evolved sets fire to the hydrogen given off from a *small* piece of potassium floating on water, the gas burning with a lilac-coloured flame: *

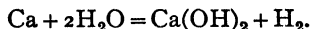


The reaction with sodium is less violent and the hydrogen does not burn:



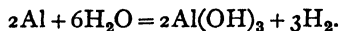
Sodium amalgam acts slowly on water and may be placed in a crucible under a gas jar full of water to collect the hydrogen.

A piece of calcium may be used in the same apparatus:

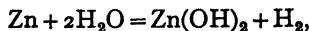


The gas obtained from calcium may contain a little acetylene, from some calcium carbide in the metal.

Cold water is decomposed by amalgamated aluminium (made by rubbing aluminium foil with damp mercuric chloride):

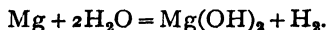


Hot water is decomposed by zinc-copper couple (made by pouring a solution of copper sulphate over granulated zinc, p. 398):

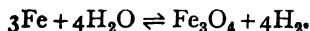
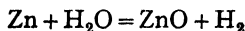
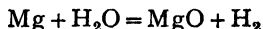


* The fused globule of caustic alkali left on the water after the action of sodium or potassium is usually thrown out of the liquid with a sharp crack on cooling, so that it is safer to place a bell-jar (open at the top) over the dish. Serious results follow the projection of the alkali into the eye or on the skin. All experiments with sodium and potassium, like those with phosphorus (p. 14), require great care. Attempts to collect the hydrogen evolved with sodium usually result in explosions.

and boiling water is slowly decomposed by magnesium powder :



Steam is decomposed by heated magnesium, zinc and iron :

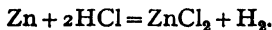
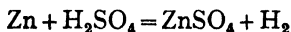


The action with magnesium has been described on p. 38; the hydrogen may be collected if the magnesium is heated in a hard glass tube and steam passed over it, but the tube usually cracks. The action of iron on steam is described on p. 38. It is reversible, so that when steam is passed over heated iron the hydrogen formed tends to reduce the oxide of iron again, and when hydrogen is passed over heated iron oxide the steam formed tends to oxidise the iron again.

When a mixture of hydrogen and steam in the correct ratio is passed over a heated mixture of iron and oxide of iron, no change occurs either in the gas or in the solid mixture, and the one mixture is therefore in chemical equilibrium with the other. The fact that such a state is possible depends on the reversibility of the reaction. *Equilibrium is attained when two opposing reactions proceed with equal speeds.* The same equilibrium state is reached by starting either with iron and steam or with iron oxide and hydrogen.

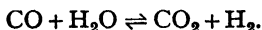
If a given weight of iron is taken and a *considerable excess* of steam passed over it, the red-hot iron will ultimately be completely oxidised; a given weight of iron oxide when heated to redness and exposed to a current of hydrogen in considerably greater amount than is required by the chemical equation will ultimately be completely reduced. This effect is sometimes called the *action of mass*.

Hydrogen from acids.—The usual *laboratory* method of preparation of hydrogen is to act upon granulated zinc in a flask or Woulfe's bottle with dilute sulphuric acid (1 vol. conc. acid to 5 vols. water) or dilute hydrochloric acid (1 vol. conc. acid to 4 vols. water), poured in through a thistle funnel (Fig. 75). Zinc sulphate or chloride is formed in solution and the hydrogen evolved is collected over water :



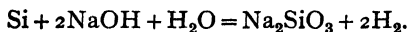
Instead of a flask a Kipp's apparatus (Fig. 23) may be used, the metal being in the central globe and acid poured in until the lower bulb is full and the metal covered. When the tap is closed evolution of gas continues until the liquid is forced by pressure partly into the upper globe and the metal is brought out of contact with the liquid, when the action ceases.

carbon monoxide is mostly converted into dioxide and more hydrogen is set free from the steam :



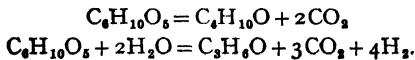
Since this reaction is reversible, excess of steam is used and a little carbon monoxide always remains in the gas. The carbon dioxide is removed by absorption in water under 25 atm. pressure and the carbon monoxide by absorption in ammoniacal cuprous formate solution under 200 atm. pressure. Large quantities of pure hydrogen are made in this way for the manufacture of synthetic ammonia (p. 473).

Hydrogen can be made on a semi-technical scale for filling military balloons (when cylinders of compressed gas are not available) by the action of hot 20 per cent. sodium hydroxide solution on silicon or ferro-silicon (an alloy of iron and silicon) rich in silicon :



The action of water on an alloy of lead and sodium or on calcium hydride has also been used.

Hydrogen is produced in certain fermentation reactions, *e.g.* along with carbon dioxide in the industrial production of butyl alcohol ($\text{C}_4\text{H}_{10}\text{O}$) and acetone ($\text{C}_3\text{H}_8\text{O}$) by the anaerobic fermentation of starch :



Hydrogen is made in California by the thermal decomposition of hydrocarbons, especially methane (natural gas) : $\text{CH}_4 = \text{C} + 2\text{H}_2$. Gases from petroleum "cracking" are also used. The methane is also mixed with steam and heated : $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$.

Uses of hydrogen.—Hydrogen is used industrially for filling balloons, as it is the lightest gas known (density relative to air = 1 is 0.069) ; coal gas is often used for balloons as it contains a good deal of hydrogen. Hydrogen is used in the synthesis of ammonia ; for "hardening" vegetable or animal oils, converting them into solid fats ; for hydrogenating petroleum fractions, coal and other organic compounds ; for lead "burning" (autogenous welding without solder, by a hydrogen flame), and in blowpipes.

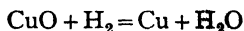
Properties of hydrogen.—Hydrogen is a colourless gas which has no smell when pure. It does not support respiration although it is not poisonous (unless it contains arsenic hydride as impurity). When breathed mixed with some air for a short time hydrogen weakens the voice and raises its pitch. Hydrogen is a better conductor of heat than other gases. Hydrogen is liquefied and solidified only with difficulty ; the gas warms rather than cools by free expansion (p. 117) unless it has

first been strongly cooled by liquid air. The liquid and solid are colourless and transparent.

Hydrogen forms compounds with a large number of elements, in many cases by direct combination: antimony, arsenic, barium, boron, bromine, calcium, carbon, chlorine, copper, fluorine, iodine, nickel, nitrogen, oxygen, palladium, phosphorus, potassium, selenium, silicon, sodium, strontium, sulphur, tellurium, and several rare metals, all form hydrides.

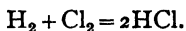
Hydrogen burns in oxygen or air to form water but does not itself support combustion, as may be shown by passing a lighted taper into an inverted jar of hydrogen burning at the mouth, when the taper is extinguished. Oxygen will also burn in hydrogen (p. 113). A mixture of hydrogen with air or oxygen explodes violently when kindled, provided either gas is not in too large excess.

By reason of its tendency to unite with oxygen, hydrogen acts as a **reducing agent**. Thus, if hydrogen is passed over many heated metallic oxides the latter are reduced to the metals (copper, iron, lead) and water is produced:

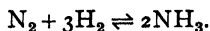


(cf. p. 136). Some very stable oxides, *e.g.* aluminium oxide, are not reduced by hydrogen.

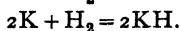
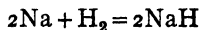
Hydrogen burns in chlorine and a mixture of hydrogen and chlorine explodes violently when kindled or exposed to bright sunlight. Hydrogen chloride is formed:



Hydrogen will unite with nitrogen on sparking or in presence of a catalyst, ammonia gas being produced:

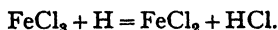


Hydrogen combines with heated sodium or potassium forming sodium or potassium hydride. These when pure are colourless salt-like substances:



Hydrogen is absorbed or *occluded* by the metal palladium: in this case also a hydride Pd_2H seems to be formed.

Nascent hydrogen.—If a little ferric chloride is added to a mixture of zinc and dilute sulphuric acid evolving hydrogen, the ferric salt is rapidly reduced to a ferrous salt, as may be found by the appropriate tests:



No such change is produced by bubbling gaseous molecular hydrogen (H_2) through the solution.

It is supposed that the peculiar activity of the hydrogen in such cases is due to the fact that it is *nascent* (new-born), *i.e.* in the act of liberation from its compounds, and that the nascent condition is due to the hydrogen being then in the state of *free atoms*, which have not time to join up to form molecules before interaction occurs. Hydrogen liberated at the cathode in electrolysis also behaves like nascent hydrogen.

The activity of nascent hydrogen may depend on the conditions in which it is formed. Potassium chlorate is not reduced by sodium amalgam, but is reduced to chloride by zinc and dilute sulphuric acid. Zinc and potassium hydroxide reduce nitrates and nitrites to ammonia, sodium amalgam reduces them to sodium hyponitrite ($\text{Na}_2\text{N}_2\text{O}_2$). Zinc amalgam is often more active than zinc, especially if a trace of copper salt is added, and copper deposited on zinc ('copper-zinc couple', see p. 398) is sometimes used as a reducing agent.

Atomic hydrogen.—Langmuir has shown that when hydrogen is strongly heated, say by contact with a tungsten wire heated by an electric current and surrounded by hydrogen gas at low pressure, its molecules are dissociated into atoms: $\text{H}_2 \rightleftharpoons 2\text{H}$. This division of the hydrogen molecule is attended by the absorption of a large amount of energy. The atomic hydrogen so formed is chemically very active. Langmuir also

showed that atomic hydrogen is formed when an electric arc is allowed to burn in hydrogen at atmospheric pressure (Fig. 77). Hydrogen gas issues from the central nozzle and is dissociated in an electric arc between two tungsten rods nearly meeting in a V. The atomic hydrogen is blown out of the arc and forms an intensely hot flame, which is capable of melting tungsten (m.pt. 3400°). This flame obtains its heat not from combustion but from the recombination of hydrogen atoms to H_2 :

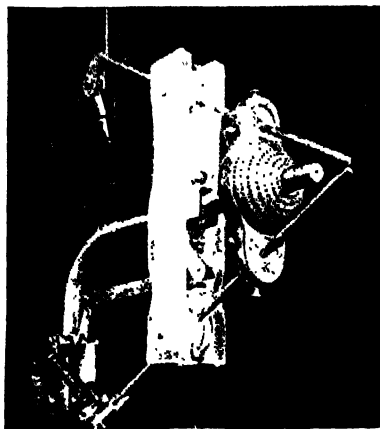
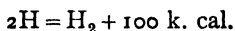


FIG. 77.—Atomic hydrogen blowpipe.

Atomic hydrogen is also formed by an electric discharge in hydrogen gas at low pressure. It combines with chlorine in the dark, forms hydrogen peroxide with molecular oxygen: $2\text{H} + \text{O}_2 = \text{H}\cdot\text{O} - \text{O}\cdot\text{H}$, and combines with sulphur and phosphorus and some metals in the cold, but does not combine with nitrogen.

Catalytic combustion.—Although oxygen and hydrogen do not combine at the ordinary temperature, a jet of hydrogen is inflamed if directed on a little platinum sponge or a bundle of fine platinum wires, which become red-hot and then kindle the hydrogen in air (Döbereiner, 1823). This is a catalytic action. The catalytic activity of the platinum in such reactions may be due to the *adsorption* on the metal of a layer of gas in an active state, and possibly in the atomic condition.

Döbereiner's lamp (Fig. 78) is a small hydrogen generator. A glass tube with a stopcock and jet at the top is held in dilute sulphuric acid. A piece of zinc hangs inside the tube and the gas generated displaces the acid until it is no longer in contact with the zinc, when action ceases. Opposite the jet is a sponge of fine platinum wire enclosed in a brass tube, and when the tap is opened the stream of hydrogen ignites. This property has been applied in automatic gas lighters, which contain fine platinum wires in a perforated brass tube. The wire fairly soon loses its activity, as it is "poisoned" by impurities in the gas. The activity of the platinum may be restored by boiling the metal with nitric acid, when the impurities are removed. Faraday observed that very clean platinum foil will bring about the combination of a mixture of hydrogen and oxygen, sometimes with explosion.

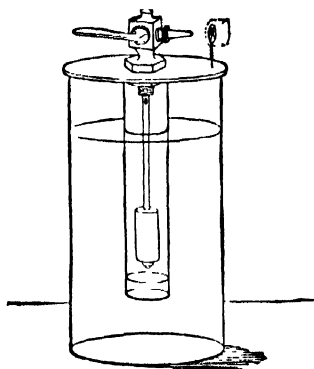


FIG. 78.—Döbereiner's lamp.

CHAPTER XIII

WATER AND HYDROGEN PEROXIDE

THE simpler experiments on the composition of water, and the subject of natural waters, have been dealt with in Chapters IV and VI, respectively. In the present chapter some methods of determining with accuracy the composition of water by weight and by volume will be considered.

The composition of water by weight.—Since it is difficult to weigh with accuracy large volumes of hydrogen and oxygen, the composition of water by weight (or the *gravimetric* composition) was first found by an indirect method, which was used by Berzelius and Dulong in 1819. A stream of dry hydrogen, which is not weighed, is passed through a weighed tube containing copper oxide heated to dull redness. The oxide is reduced by the hydrogen to metallic copper, the oxygen of the oxide uniting with the hydrogen to form water which passes off in the form of vapour, which is collected in a weighed calcium chloride tube and weighed :

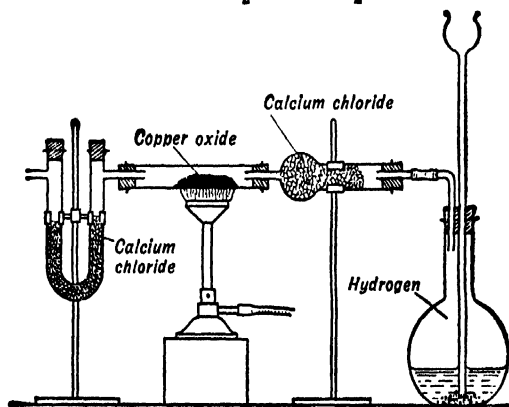
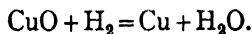


FIG. 79.—Composition of water by weight.

The tube containing the copper is then allowed to cool and weighed. From the results we find :

Loss of weight of copper oxide = weight of oxygen = o ;
Weight of water - weight of oxygen = weight of hydrogen = h ;
 \therefore ratio of combining weights = o/h .

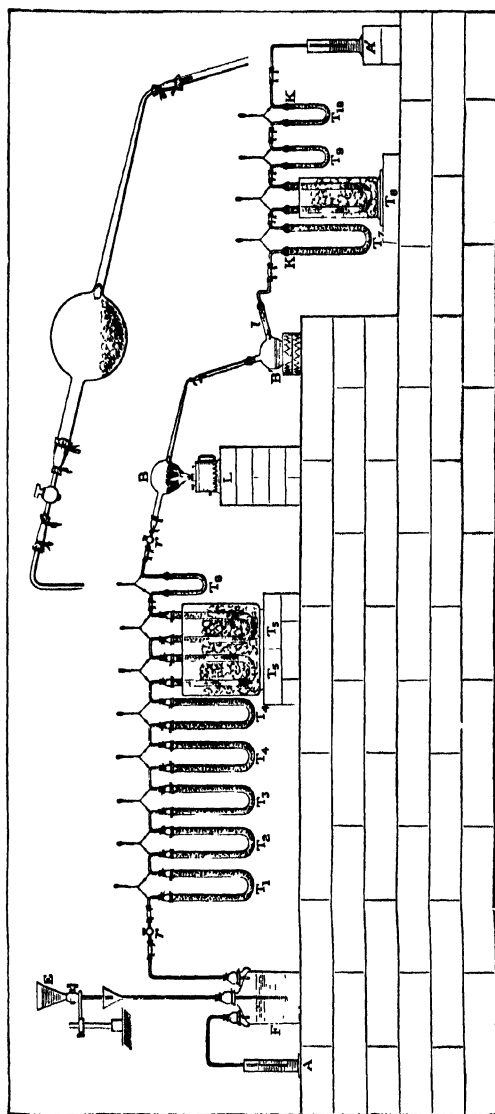


FIG. 80.—DUMAS' APPARATUS.

The apparatus shown in Fig. 79 may be used. (It is better to have an empty bulb between the copper oxide tube and the calcium chloride tube and weighed with the latter, in order to collect some of the water in the liquid state.) It will be found that about 8 parts of oxygen combine with 1 part of hydrogen.

Dumas' experiment.—This method was used by Dumas in 1842 with the apparatus shown in Fig. 80. The hydrogen was prepared from zinc and dilute sulphuric acid and was purified by reagents in several U-tubes. Hydrogen sulphide was removed by lead nitrate, arsenic hydride by silver sulphate, acid vapours by caustic potash, and water by sulphuric acid cooled in ice (when reaction with hydrogen is negligible) or phosphorus pentoxide. The *témoin* tubes should remain of constant weight, showing that the drying agents are acting as efficiently as possible. The rest of the apparatus is described below the illustration.*

Morley's experiments.—Some very accurate experiments on the composition of water by weight were made by the American chemist E. W. Morley from 1880 to 1895. Purified oxygen and hydrogen gases were weighed in large glass globes; in the later experiments the hydrogen was weighed in a bulb containing palladium, which has the unique property of absorbing large volumes of hydrogen but not other gases. When the palladium charged with hydrogen is strongly heated pure hydrogen is evolved. The gases were burnt at platinum jets in a previously evacuated sealed glass vessel (Fig. 81) immersed in cold water. The water collecting in this tube was then frozen, and the residual gas pumped out through a tube containing phosphorus pentoxide (to keep back water vapour) and analysed.

As a final result, the mean of twelve experiments in which 400 gm. of water were produced, Morley obtained the ratio :

oxygen : hydrogen = 7.9396 : 1,

and if the atomic weight of oxygen is 16 this gives the atomic weight of hydrogen as $H = 16 \div (2 \times 7.9396) = 1.00673$.

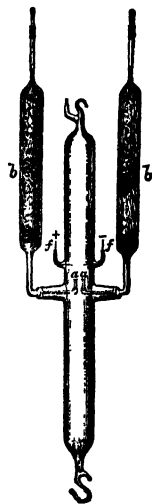


FIG. 81.—Morley's apparatus. The dry gases passed through phosphorus pentoxide tubes, *b, b*, to the jets, *a, a*, where they were ignited by electric sparks between wires from the electrodes, *f* and *f*.

* A full account of the experiments on the composition of water discussed in this chapter (except those of Noyes) will be found in Partington, *The Composition of Water*, 1928. Noyes's paper is in *J. Amer. Chem. Soc.*, 1907, 29, 1718.

Noyes' experiments.—In 1907 W. A. Noyes improved a method he had used in 1890 for the determination of the atomic weight of hydrogen. In one set of experiments, pure hydrogen was absorbed in palladium in an exhausted tube which was weighed. Pure oxygen was then admitted and the tube heated, when the hydrogen in the palladium burned to steam which condensed to liquid water in a cooled extension limb of the tube. The tube and water were then weighed and connected with an apparatus in which the water was collected and weighed, the residual gas being pumped off and measured, and its weight applied in correcting the result. Noyes also used copper oxide in the tube and admitted pure hydrogen to it. The results for copper oxide gave somewhat lower numbers; those for palladium and the purest hydrogen (from electrolysis of baryta solution), which Noyes considered the best, gave

$$H = 1.00787.$$

Scott's experiments.—Accurate measurements of the volumetric combining ratio of hydrogen and oxygen were made by Scott (1893). The apparatus (Fig. 82) consisted of a pipette *A* in which gas was

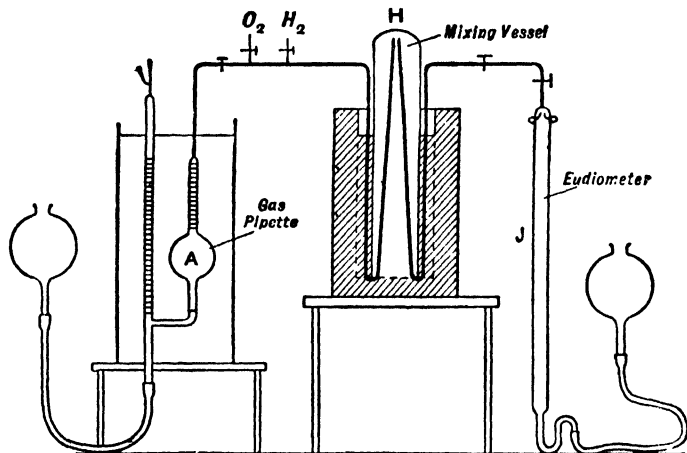


FIG. 82.—Scott's apparatus.

measured and passed into a mixing container *H* over mercury. Pure oxygen was obtained by heating silver oxide, pure hydrogen by the action of steam on sodium. The mixed gas was exploded in portions by sparking in the eudiometer *J* and the residual gas measured in *A*. In this way the volume ratio hydrogen : oxygen = 2.00285 at S.T.P. was found.* Burt and Edgar (1916) †, in a very elaborate and accurate research, found

* Moles has recalculated Scott's value as 2.00302; *Z. physikal. Chem.*, 1925, 115, 61; 117, 157.

† *Phil. Trans.*, 1916, 216, 393.

2.00288. With Morley's values for the normal densities of hydrogen (0.089873 gm./lit.) and oxygen (1.42900 gm./lit.) this gives

$$H = 2.00288 \times 0.089873 \times 8 / 1.42900 = 1.00773.$$

The mass spectrograph (p. 258) gives the value 1.0080.

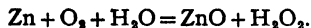
HYDROGEN PEROXIDE

History.—Hydrogen peroxide was discovered by Thenard in 1818*; he obtained it by the action of dilute acids on barium peroxide and called it *oxygenated water*, since he showed that its formula corresponded to H_2O_2 .

Occurrence.—Hydrogen peroxide vapour occurs in traces in the atmosphere and traces of hydrogen peroxide are said to be formed in plants.

Preparation.—Hydrogen peroxide is *formed* in small quantities in the combustion of hydrogen: $H_2 + O_2 = H_2O_2$. This may be demonstrated by allowing a hydrogen flame to play on a piece of ice and adding to the water formed a solution of titanium dioxide in sulphuric acid; a yellow colour develops, which is a sensitive test for hydrogen peroxide.

Hydrogen peroxide is formed when certain metals such as zinc, or oxidisable organic substances such as turpentine, oxidise on exposure to air in presence of water. This may be shown by adding some turpentine to a dilute solution of potassium iodide containing starch, and shaking. On allowing the mixture to stand in a flask, a blue colour due to liberation of iodine by hydrogen peroxide develops: $2KI + H_2O_2 = 2KOH + I_2$. These reactions are examples of **autoxidation**, in which a substance oxidised by gaseous oxygen in presence of water gives rise to the formation of hydrogen peroxide, the oxygen being divided equally between the substance oxidised and the water:

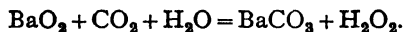


Hydrogen peroxide is formed by the combination of atomic hydrogen with the oxygen molecule, either by mixing gaseous atomic hydrogen (p. 134) with oxygen or by bubbling oxygen under pressure past the cathode from which hydrogen is being evolved in electrolysis, when atomic hydrogen (*nascent hydrogen*) is first set free: $2H + O_2 = H_2O_2$.

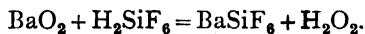
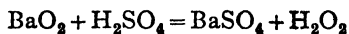
Hydrogen peroxide is *prepared* by the action of an acid on a suitable metallic peroxide. To obtain a solution of hydrogen peroxide free from metallic salts, barium peroxide is used with an acid which forms an insoluble barium salt, such as carbonic, sulphuric or hydrofluosilicic acid. Potassium peroxide and tartaric acid may be used, when potassium hydrogen tartrate is precipitated.

* See "Eau oxygénée et ozone", *Classiques de la Science*, III (A. Colin, Paris). Note "Thenard" not "Thénard".

By passing carbon dioxide into a suspension of barium peroxide in distilled water, barium carbonate is precipitated and a solution of hydrogen peroxide may be filtered from the barium carbonate :

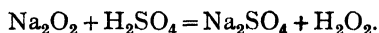


Anhydrous barium peroxide is not easily acted upon by dilute sulphuric acid since the particles become coated with insoluble barium sulphate. The hydrated barium peroxide $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ is easily decomposed with cold dilute sulphuric acid (1 vol. of acid to 5 vols. of water) or with hydrofluosilicic acid :



Barium peroxide also hydrates slowly when stirred with water and can then be decomposed by dilute sulphuric acid. This method is used on the large scale. The barium sulphate precipitate is a valuable by-product used as a pigment (*blanc fixe*).

Sodium peroxide added in small portions to 20 per cent. sulphuric acid cooled on ice reacts as follows :



Solutions of hydrogen peroxide are much more stable if a little sulphuric or phosphoric acid is present.

The strength of hydrogen peroxide solutions is stated in terms of the volume of oxygen evolved on heating, when the peroxide decomposes : $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$. Commercial peroxide is usually 10 volumes or 20 volumes, according as it gives off 10 or 20 times its volume of oxygen. From the equation it is seen that 2×34 gm. of hydrogen peroxide evolve 32 gm. of oxygen, occupying 22.4 litres at S.T.P. Thus each gram of peroxide evolves 329.4 c.c. of oxygen. A 1 per cent. solution evolves 3.294 times its volume of oxygen ; 10 vol. peroxide is 3.04 per cent. strength. A stronger solution on the market is "100 vol." or 30 per cent.

A solution of hydrogen peroxide may be concentrated : (i) By freezing, when ice separates and the residual liquid is enriched in peroxide. (ii) By evaporation on a water bath, as hydrogen peroxide is appreciably less volatile than water ; at a certain point, however, decomposition begins. (iii) By exposing the solution in a flat dish in an exhausted desiccator containing concentrated sulphuric acid ; when a certain concentration of peroxide is reached the latter begins to volatilise, but by working at low temperatures Thenard was able to obtain a liquid (sp. gr. 1.452) giving off 475 vols. of O_2 at 14° , i.e. containing 95 per cent.

of H_2O_2 . (iv) By distillation under reduced pressure; this method was also used by Thenard. In 1894 Wolfenstein obtained practically pure hydrogen peroxide by the fractional distillation of a concentrated aqueous solution under reduced pressure.

The apparatus used for distillation under reduced pressure (Fig. 83) consists of a distilling flask containing the solution of hydrogen peroxide

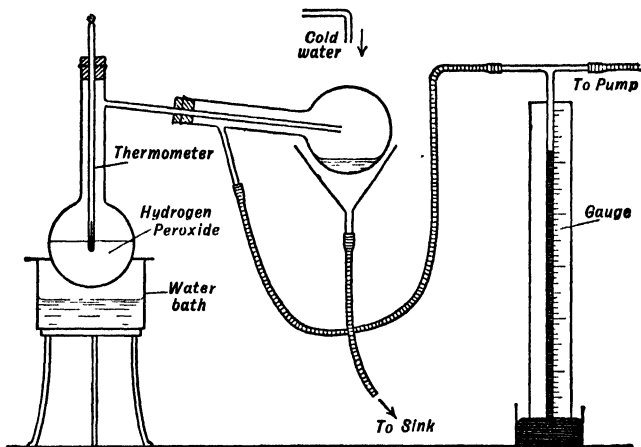
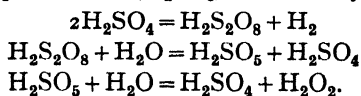


FIG. 83.—Distillation under reduced pressure.

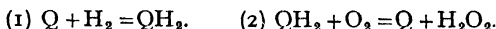
placed on a water bath. The side tube is fitted by a rubber stopper to the inside of a second distilling flask, which serves as a receiver and is cooled by a stream of cold water. The side tube of this flask communicates by pressure tubing with a pressure gauge and a large empty bottle which is connected with a good water pump. A three-way stopcock allows air to be admitted to the apparatus when the receiver is changed. At first water comes over, since hydrogen peroxide has a higher boiling point. The later fraction is collected and redistilled under reduced pressure, when almost pure hydrogen peroxide may be obtained.

Hydrogen peroxide is now manufactured in pure 30 or even nearly 100 per cent. solution by the electrolysis of 50 per cent. sulphuric acid, followed by vacuum distillation in a special apparatus. Persulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) is formed by electrolysis and on distillation this reacts with water to form first permonosulphuric acid (H_2SO_5) and then hydrogen peroxide :



In a new process ethyl anthraquinone (Q) in an organic solvent is reduced by hydrogen in presence of palladium as a catalyst to ethyl anthraquinol (QH_2). The solution is exposed to air, when ethyl anthraquinone

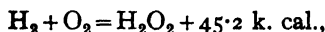
and hydrogen peroxide are formed. The hydrogen peroxide is extracted with water and purified by distillation under reduced pressure :



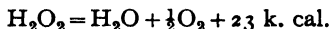
An 85-90 per cent. H_2O_2 is used as fuel for rocket motors and guided weapons, as a torpedo propellant, and for submarine motors.

Properties.—Pure hydrogen peroxide is a clear, syrupy liquid, sp. gr. 1.465 at 0° , colourless in small amounts but having a bluish colour in bulk. It has an odour like that of nitric acid and a harsh metallic taste, and it blisters the skin. It freezes when cooled, m.pt. -0.46° . When rapidly heated to 150° it explodes violently. The pure liquid has a strong *acid* reaction to litmus but in *pure* dilute solution hydrogen peroxide is quite neutral. The pure peroxide is fairly stable and can be kept for several weeks in the absence of sunlight, provided the glass of the bottle is perfectly smooth. In contact with rough surfaces or on shaking, decomposition occurs : $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$. Finely divided metals such as gold, silver and platinum (but not iron) cause explosive decomposition. Cotton wool at once inflames. By mixing the pure peroxide with water and cooling in a mixture of solid carbon dioxide and ether, the crystalline hydrate $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ is obtained.

Hydrogen peroxide is formed *from its elements* with evolution of heat :



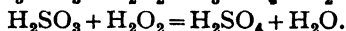
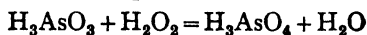
but decomposes into oxygen and water with evolution of heat :



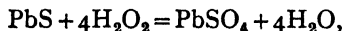
It is unstable at the ordinary temperature, tending to pass into water and oxygen.

Hydrogen peroxide forms addition compounds with some salts, *e.g.* $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$, and with urea, $\text{CON}_2\text{H}_4 \cdot \text{H}_2\text{O}_2$, and in these compounds it behaves like water of crystallisation.

Hydrogen peroxide is an *active oxidising agent*, an oxygen atom being easily removed, with formation of water. Arsenious and sulphurous acids are oxidised to arsenic and sulphuric acids :



Black lead sulphide is oxidised to white lead sulphate :

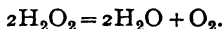


a reaction utilised in restoring discoloured oil paintings in which the white-lead pigment (basic lead carbonate) has been blackened by atmospheric hydrogen sulphide. Ferrous salts in acid solution are oxidised to ferric salts :

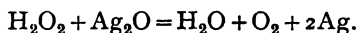


The oxidising action is used in bleaching delicate materials (wool, silk, ivory, feathers) which would be injured by chlorine ; the solution of the peroxide is made faintly alkaline with ammonia or added to 10 per cent. sodium acetate solution. Hydrogen peroxide bleaches hair to a golden-yellow colour. It is also an antiseptic, and as it leaves no injurious products after its action it is largely used as a gargle, etc.

Platinum black and especially colloidal platinum (prepared by striking electric arcs between platinum wires under distilled water), bring about a rapid catalytic decomposition of hydrogen peroxide :

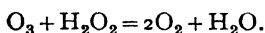


In certain reactions hydrogen peroxide appears to act as a *reducing agent*. Thenard (1819) found that gold and silver oxides are reduced to the metals :

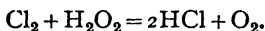


Brown silver oxide is precipitated by sodium hydroxide solution from silver nitrate solution and hydrogen peroxide solution added. There is a brisk effervescence of oxygen and the solid is converted into black metallic silver. A further quantity of H_2O_2 added is *catalytically* decomposed by the finely divided silver.

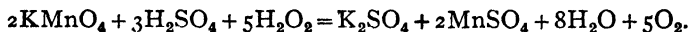
Hydrogen peroxide slowly reduces ozone to oxygen :



Hydrogen peroxide is used as an *antichlor* to remove excess of chlorine from bleached fabrics :

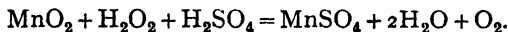


A solution of potassium permanganate acidified with sulphuric acid is readily reduced and decolorised by hydrogen peroxide, with evolution of oxygen :

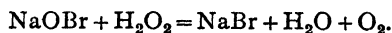


This reaction is used in the titration of hydrogen peroxide solutions, the permanganate being added from a burette.

Manganese dioxide liberates oxygen from a *neutral* solution of hydrogen peroxide, the action being apparently catalytic, but in *acid* solution the manganese dioxide is reduced to a manganous salt and twice as much oxygen is evolved as from a neutral solution :



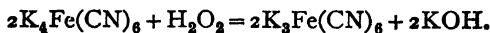
Solutions of bleaching powder and sodium hypobromite evolve oxygen :



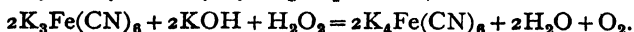
These reactions are also applied in the estimation of hydrogen peroxide.

An interesting case of the oxidising and reducing action of hydrogen peroxide was discovered by Brodie. An *acid* solution of potassium

ferrocyanide is *oxidised* by hydrogen peroxide to potassium *ferricyanide* :



An *alkaline* solution of potassium *ferricyanide*, however, is *reduced* to potassium *ferrocyanide* by hydrogen peroxide, with evolution of oxygen :



Tests for hydrogen peroxide.—Hydrogen peroxide may be detected by the liberation of iodine from potassium iodide, giving a blue colour with starch. Other substances, such as ozone and nitrites, give this reaction. The liberation of iodine occurs somewhat slowly but is rapid in presence of ferrous sulphate : $2\text{KI} + \text{H}_2\text{O}_2 = 2\text{KOH} + \text{I}_2$.

A delicate test is the formation from chromium trioxide CrO_3 of a deep blue so-called "perchromic acid" CrO_5 . A *dilute* solution of potassium dichromate acidified with sulphuric acid is added to a dilute solution of hydrogen peroxide in a stoppered cylinder. The solution is rapidly shaken with ether, which floats to the surface with a beautiful blue colour : this solution slowly decomposes and a bluish-green solution of chromic sulphate is formed in the water layer.

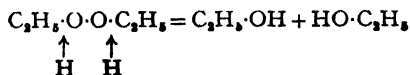
The most delicate reaction for hydrogen peroxide is the formation of a yellow colour, due to titanium peroxide TiO_3 , with a solution of titanium dioxide in dilute sulphuric acid. This solution is prepared by heating TiO_2 with twice its volume of concentrated sulphuric acid, cooling, and diluting with ice-water.

Formula of hydrogen peroxide.—The vapour density of hydrogen peroxide as determined under reduced pressure at 90° is 17 ; the molecular weight has also been found from the freezing point of the aqueous solution (p. 214) as 34 ; hence the formula is H_2O_2 .

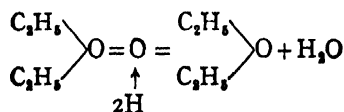
The constitutional formula may be $\text{H}\cdot\text{O}\cdot\text{O}\cdot\text{H}$, *i.e.* dihydroxyl, $\text{HO}\cdot\text{OH}$. This is in accordance with the instability of compounds which contain chains of directly linked oxygen atoms.

In order to account for the instability of one oxygen atom, which suggests that it is linked differently from the other, Kingzett (1884) wrote the formula as $\text{O}=\text{O}=\text{H}_2$, in which one oxygen is quadrivalent. In the modern theory of valency the maximum covalency of oxygen is three, and this formula would have to be written as $[\text{O}=\text{O}-\text{H}]^-\text{H}^+$, a weak acid.

By the action of hydrogen peroxide on diethyl sulphate $(\text{C}_2\text{H}_5)_2\text{SO}_4$, Baeyer and Villiger (1900) obtained diethyl peroxide $(\text{C}_2\text{H}_5)_2\text{O}_2$, and by the action of zinc and acetic acid this is reduced to ethyl alcohol $\text{C}_2\text{H}_5\cdot\text{OH}$. This agrees with the formula $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{O}\cdot\text{C}_2\text{H}_5$:



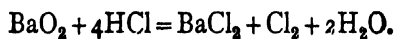
Kingzett's formula would require that ether $(C_2H_5)_2O$ should be formed :



H_2O_2 is a *true peroxide* containing two singly linked oxygen atoms :
 $H-O-O-H$. Sodium peroxide is $Na-O-O-Na$ and barium

peroxide $Ba \begin{array}{c} \diagup O \\ \diagdown O \end{array}$. True peroxides give hydrogen peroxide with dilute

acids and differ from the *dioxides* of lead, manganese, etc., which are insoluble in dilute acids but give oxygen with concentrated sulphuric acid and chlorine with concentrated hydrochloric acid. Their formulae are of the type $O=Pb=O$. This is confirmed by the formation of unstable higher chlorides on treatment with cold concentrated hydrochloric acid, *e.g.* $PbCl_4$. With concentrated hydrochloric acid barium peroxide evolves chlorine (Brodie, 1863) :



CHAPTER XIV

CHLORINE

History.*—In 1648 Glauber obtained a strongly acid "spirit of salt" by heating moist salt in a charcoal furnace and condensing the fumes in receivers. In 1658 he obtained "spirit of salt" by distilling common salt with concentrated sulphuric acid and dissolving the evolved gas in water. The other product of the reaction was sodium sulphate, called Glauber's salt. In 1772 Priestley found that the gas could be collected over mercury but was very soluble in water. The solution was spirit of salt, which was then called **muriatic acid**. Lavoisier (1789) regarded it, like other acids, as the oxide of a non-metallic element then unknown and called by him the **muriatic radical**.

In 1774 Scheele had examined the action of concentrated muriatic acid on "black manganese" or manganese dioxide. This dissolved in the cold to form a dark-brown solution, which on warming gave off a greenish-yellow gas which had a powerful odour and bleached vegetable colours. Scheele said this gas was muriatic acid deprived of phlogiston by the manganese, and since he thought hydrogen was phlogiston, this means muriatic acid deprived of hydrogen, which is correct.

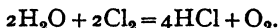
In 1786 Berthollet exposed a solution of the gas in water to light, when it gave off bubbles of oxygen and left a solution of muriatic acid. In accordance with Lavoisier's theory, he considered that the gas was a compound of muriatic acid and oxygen, or **oxymuriatic acid**.

The production of oxymuriatic acid by the action of oxidising agents (e.g. manganese dioxide) on muriatic acid seemed to show that oxymuriatic acid was a higher oxide of the muriatic radical, and Berthollet's experiment also supported this hypothesis. All that remained was to isolate the muriatic radical and this was regarded as a task for the future.

In 1810 Davy tried to decompose oxymuriatic acid into oxygen and the muriatic radical. He burnt phosphorus in the gas, expecting to get phosphorus pentoxide, but the products were a volatile liquid (phosphorus trichloride) and a solid (phosphorus pentachloride) quite different from phosphorus pentoxide. On heating sulphur in the gas he did not obtain sulphur dioxide but a liquid (chloride of sulphur). Charcoal even when heated at a very high temperature (the electric arc) in the gas did not form any carbon dioxide but was entirely without action.

* See *Alembic Club Reprints* Nos. 9 and 13.

Since all the products obtained from "oxymuriatic acid" weighed more than the gas, and since no compounds known to contain oxygen were ever produced from it, Davy concluded that "oxymuriatic acid" is really an element, and all its reactions could be explained by this. He called oxymuriatic acid *chlorine*, derived from the Greek *chloros* = pale green. Muriatic acid is a compound of hydrogen and chlorine, and should be called hydrochloric acid. Davy showed that in Berthollet's experiment the oxygen came from the water, the hydrogen of which united with the chlorine to form hydrochloric acid :



He found that *dry* chlorine does not bleach and the bleaching action is due to nascent oxygen liberated from the water which must be present.

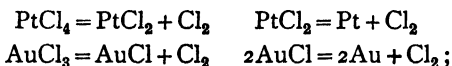
This may be shown by hanging a piece of dry red flannel in a jar of chlorine dried by concentrated sulphuric acid. The colour is not bleached. If the flannel is taken out, wetted, and put back into the chlorine, the colour is bleached.

The production of chlorine from muriatic acid and higher oxides (*e.g.* manganese dioxide) is explained by the union of some of the oxygen of the higher oxide with the hydrogen of the acid, setting free the chlorine :

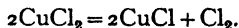


This may be shown by passing dry hydrogen chloride gas over some dry manganese dioxide heated in a bulb tube, when chlorine is evolved and moisture condenses on the cool part of the tube.

Preparation.—Chlorine is evolved when gold, platinum and cupric chlorides are heated ; lower chlorides of platinum and gold are first produced but decompose at higher temperatures :

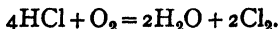


cupric chloride decomposes into chlorine and the stable cuprous chloride :

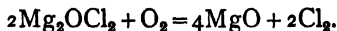


Pure chlorine has been prepared by the electrolysis of fused silver chloride with carbon electrodes : $2\text{AgCl} = 2\text{Ag} + \text{Cl}_2$.

Hydrogen chloride gas is oxidised by *free* oxygen when the mixture is passed over a heated catalyst (p. 151) :



✓ Chlorine is also formed by passing air over strongly heated magnesium oxychloride (p. 333) :



The common *laboratory method* for the preparation of chlorine is to heat a mixture of manganese dioxide and concentrated hydrochloric acid in a flask (Fig. 84) :



The reaction probably takes place in two stages ; a higher chloride of manganese MnCl_3 is first formed in the cold as a dark-brown solution,

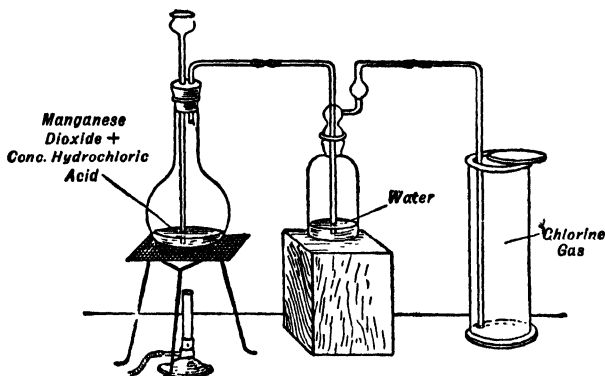
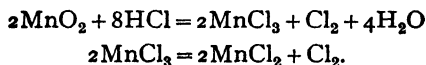


FIG. 84.—Preparation of chlorine.

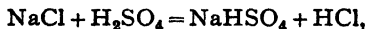
which decomposes on heating with the evolution of chlorine and the formation of manganous chloride MnCl_2 :



The gas is washed with a little water to free it from hydrochloric acid and is collected in dry jars by downward displacement, since it is more than twice as heavy as air and is fairly soluble in water. It attacks mercury.

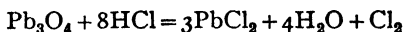
Chlorine has a powerful action on the mucous membranes and the experiment is best performed in a fume cupboard. The gas may also be collected over a saturated solution of common salt. It may be dried by calcium chloride or concentrated sulphuric acid.

Instead of using hydrochloric acid, a mixture of common salt, manganese dioxide and 50 per cent. sulphuric acid may be heated, when hydrochloric acid is first produced :

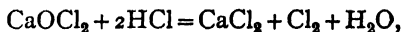


and is then oxidised by the manganese dioxide. This mixture evolves a slow stream of chlorine in the cold.

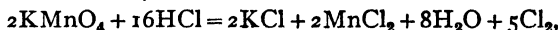
Chlorine is evolved when hydrochloric acid is heated with red lead or lead dioxide :



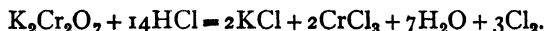
and by dropping cold concentrated hydrochloric acid on bleaching powder :



or on potassium permanganate :

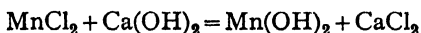


or by heating concentrated hydrochloric acid with potassium dichromate

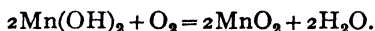


Pure chlorine may be obtained by drying with concentrated sulphuric acid the chlorine obtained from hydrochloric acid and potassium permanganate, liquefying it in a bulb immersed in a mixture of solid carbon dioxide and ether, and then evaporating the liquid chlorine. Pure chlorine is completely absorbed by mercury, even if the materials are very dry (see p. 154).

The Weldon process.*—Chlorine was formerly obtained on the technical scale from manganese dioxide and the hydrochloric acid obtained in the Leblanc process (*q.v.*) by heating them with steam in stone tanks. To recover the manganese from the residual liquor, **Weldon's process** was used. **An excess** of milk of lime was added to precipitate manganous hydroxide :

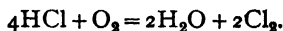


and leave excess of calcium hydroxide in suspension. The liquid was then heated by steam, and air blown through. *In presence of excess of lime* the manganous hydroxide oxidises to manganese dioxide :



This is a weakly acidic oxide and combines with lime to form a precipitate of calcium manganite CaO, MnO_2 . Some more manganese liquor was then added and the air blowing continued, when the CaO, MnO_2 was converted into $\text{CaO}, 2\text{MnO}_2$, called *Weldon mud*. This was decomposed by hydrochloric acid to give chlorine, and the above process repeated.

The Deacon process.—Hydrogen chloride gas is oxidised by *free* oxygen when a mixture of air and hydrogen chloride is passed over a heated catalyst containing cupric chloride :



* On the industrial preparation of chlorine, see Partington, *The Alkali Industry*, 1925.

A stream of air is passed through concentrated sulphuric acid in a Woulfe's bottle, into which concentrated hydrochloric acid is allowed to drop slowly. The mixture of air and hydrochloric acid gas is passed through a hard glass tube packed with pieces of pipe-clay or pumice which have been soaked in a solution of cupric chloride and dried, and the tube is heated in a furnace (Fig. 85). The gas may be passed through litmus solution, which is bleached.

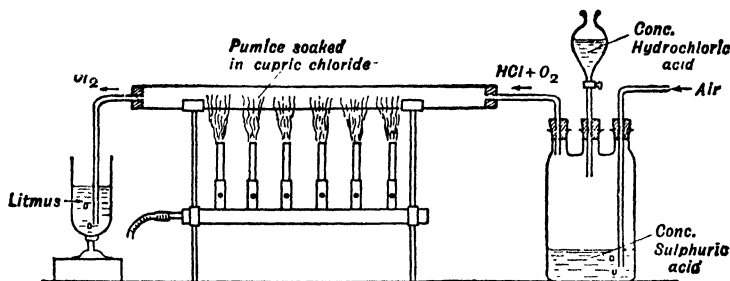
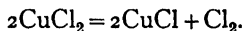


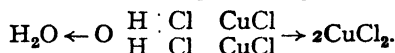
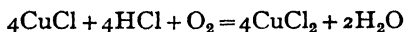
FIG. 85.—Principle of the Deacon process.

This reaction was used on the large scale as the **Deacon process** (the reaction was used by Deacon in 1868). It is not a convenient laboratory method, since the chlorine obtained is largely diluted with atmospheric nitrogen.

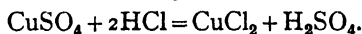
The catalytic action of the copper salt has been explained as follows. The cupric chloride decomposes on heating to form cuprous chloride and chlorine:



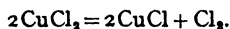
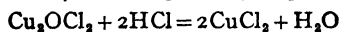
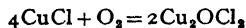
In presence of oxygen and cuprous chloride the hydrogen chloride is decomposed to form water and cupric chloride, and the reaction then begins again:



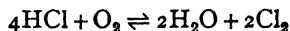
Copper sulphate if used as a catalyst is first converted into the chloride:



It is sometimes assumed that an oxychloride of copper is formed:



Since the reaction



is reversible there is always some hydrogen chloride mixed with the chlorine, and in the Deacon process this is removed by washing with

water. The gas is then dried with sulphuric acid and used to make bleaching powder (p. 164) ; it contains only 5 to 7 per cent. of chlorine.

On the large scale hydrogen chloride from salt cake furnaces (p. 156) is purified by dissolving in water and expelling the pure gas from the solution by mixing with concentrated sulphuric acid and blowing out with a current of air. The mixture of air and hydrogen chloride then passes over pieces of broken bricks impregnated with a little cupric chloride and heated at 450° in a converter divided into compartments, so that a portion of the mass can be removed and replaced when it loses its catalytic activity.

The Weldon process was invented in 1866 and soon came into large-scale operation. The Deacon process was patented in 1868 but at first gave great difficulties ; it then came into large-scale operation and partly displaced the Weldon process. Electrolytic processes could not compete with these two until the dynamo had been perfected, although a patent had been taken out by Charles Watt in 1851 for the preparation of chlorine by the electrolysis of common salt. Although the electrolytic processes were used on the large scale in Germany from 1890, it is only fairly recently that they have almost completely replaced both the Weldon and the Deacon processes.

Electrolytic processes.—Nearly all the chlorine used technically is now obtained by the electrolysis of a solution of common salt. Chlorine is liberated at the positive electrode or anode, which is usually made of carbon since this is not attacked by chlorine, which is evolved as gas and is collected. The reaction at the negative electrode or cathode depends on the arrangement of the cell. If the cathode is of iron, hydrogen is evolved

from it and a solution of sodium hydroxide is formed. In this case some arrangement, such as a porous diaphragm, must be used to prevent the chlorine formed at the anode from reacting with the sodium hydroxide formed at the cathode (see p. 161). If the cathode is of mercury, sodium is deposited on it and sodium amalgam is formed. Two typical cells may be described.

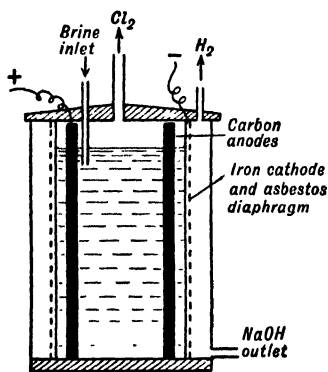


FIG. 86.—The Gibbs cell.

of which a solution of sodium hydroxide forms. This runs off and is collected. The brine level inside the cell must be kept up. The sodium hydroxide solution contains some undecomposed sodium chloride, which

The Gibbs cell (Fig. 86) has carbon rods as anodes, separated by a diaphragm of asbestos paper from the cylindrical perforated iron cathode, on the outside

separates as solid when it is concentrated (see p. 280). The chlorine evolved at the anodes is led off and collected.

The Solvay cell (Fig. 87) has a mercury cathode. The sodium chloride is decomposed into chlorine gas which is evolved from the carbon anodes and collected, and sodium which is deposited on the mercury and

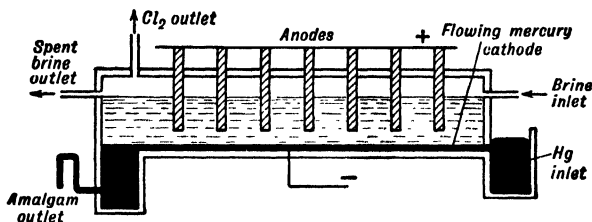


FIG. 87.—The Solvay cell.

forms sodium amalgam. The layer of mercury forming the cathode flows slowly over the slate base of the cell, which slopes as shown, and the salt brine flows in the same direction. The sodium amalgam runs out into a vessel of water containing iron rods in contact with the amalgam. This arrangement behaves as a short-circuited cell, sodium passing into solution as sodium hydroxide and hydrogen is evolved on the iron (see p. 209). Since the sodium amalgam is separated from the sodium chloride solution before it reacts with water, the solution of sodium hydroxide obtained is pure.

Most of the chlorine is used for bleaching and in refining petroleum, either as such or (usually) as *hypochlorites* of sodium or calcium, the latter in the form of *bleaching powder*. Some is used to make synthetic hydrochloric acid (p. 157), in making solvents (chlorinated acetylene, p. 403), for chlorinating water supplies (p. 57), liberating bromine from sea water (p. 178), and making some chemicals such as carbonyl chloride and sulphur chloride.

Electrolytic chlorine is fairly easily liquefied by cooling and compression. The liquid is transported in cylinders or tank wagons of steel, since this metal is not attacked by *dry* chlorine.

Properties of chlorine.—Chlorine is a greenish-yellow gas with a most irritating odour and a violently corrosive action on the mucous membranes. It is fairly easily liquefied by compression and cooling, forming an amber-yellow liquid. When cooled in liquid air this forms a pale yellow solid. Chlorine gas is fairly soluble in water and since it is heavier than air it is collected by displacement.

Chlorine is a *very active element*, combining readily with hydrogen and directly with most metals and non-metallic elements except nitrogen,

oxygen and carbon. Combination may occur when the elements are brought together at the ordinary temperature, often with the production of flame or incandescence.

The reactions with metals, *e.g.* sodium, copper and zinc, which occur violently with the moist gas do not always take place if the chlorine is *dry*, although dry chlorine reacts with phosphorus, arsenic and antimony, and pure dry mercury completely absorbs pure dry chlorine.

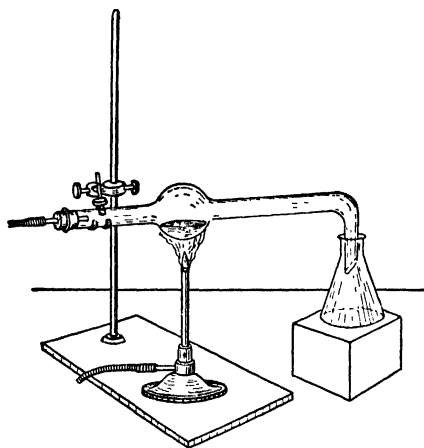


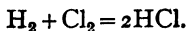
FIG. 88.—Burning sodium in chlorine.

A little finely powdered arsenic or antimony sprinkled into a jar of chlorine burns, producing *poisonous* fumes of the chlorides AsCl_3 and SbCl_5 , respectively.

A piece of phosphorus in a deflagrating spoon ignites spontaneously in chlorine, burning with a pale flame and producing fumes of the chlorides PCl_3 and PCl_5 .

When chlorine is passed over sodium heated in a hard glass bulb tube (Fig. 88), the metal burns with an exceedingly brilliant yellow flame, producing white sodium chloride NaCl .*

A jet of hydrogen burning in air continues to burn with an enlarged grey flame when introduced into a jar of chlorine, and the hydrogen chloride formed fumes in moist air :



A jet of chlorine burns with a curious needle-shaped flame when introduced into an inverted jar of hydrogen burning at the mouth.

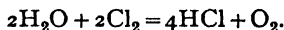
A mixture of almost equal volumes of hydrogen and chlorine is obtained by the electrolysis of hydrochloric acid (sp. gr. 1.1) with rods of carbon as electrodes (chlorine attacks platinum). The acid is in a bottle and the electrodes and delivery tube are fitted through the rubber stopper. The gas is washed with a little water in a bulb tube. The experiment is carried out in a darkened room with a ruby lamp. After half an hour the acid is saturated with chlorine and the gas may be collected in *thin* glass bulbs, *carefully* sealed off with a small flame.

A mixture of equal volumes of hydrogen and chlorine explodes violently when kindled by a taper, or when the mixture in a thin glass bulb is exposed

* As the sodium may not be completely burnt, care should be taken in adding water to the tube after the experiment. A little methylated spirit put in first will remove the sodium with safety.

to bright sunlight or to the light of burning magnesium. Combination occurs slowly when the mixture is exposed to diffused daylight but the gases do not react in the dark.

Chlorine has a great *affinity for hydrogen* and will remove it from many compounds. It will remove hydrogen from water, setting free the oxygen :



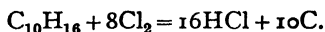
This reaction takes place when steam and chlorine are passed through a heated tube (p. 106), or when chlorine water (a solution of chlorine in water) is exposed to sunlight in an inverted flask, when bubbles of oxygen are evolved and a solution of hydrochloric acid remains.

Chlorine also removes hydrogen from compounds of carbon and hydrogen, setting free the carbon. A burning taper burns in a jar of chlorine with a small dull-red flame, clouds of black carbon and fumes of hydrochloric acid being evolved. Paraffin wax is a mixture of hydrocarbons or compounds of carbon and hydrogen. The chlorine removes the hydrogen forming hydrogen chloride and sets free the carbon, with which it does not combine directly.

A mixture of 2 vols. of chlorine and 1 vol. of methane gas CH_4 when kindled burns, giving fumes of hydrochloric acid and a cloud of carbon : $\text{CH}_4 + 2\text{Cl}_2 = \text{C} + 4\text{HCl}$.

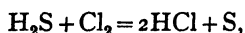
A mixture of 2 vols. of chlorine and 1 vol. of ethylene gas C_2H_4 when kindled burns with a red flame, emitting fumes of hydrochloric acid and a dense black cloud of carbon : $\text{C}_2\text{H}_4 + 2\text{Cl}_2 = 2\text{C} + 4\text{HCl}$.

A little turpentine poured on filter paper catches fire when plunged into chlorine, giving a black cloud of carbon and fumes of hydrochloric acid :

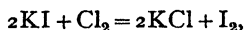


Chlorine combines with sulphur dioxide SO_2 , carbon monoxide CO , and ethylene C_2H_4 , producing sulphuryl chloride SO_2Cl_2 , carbonyl chloride (*phosgene*) COCl_2 , and ethylene dichloride $\text{C}_2\text{H}_4\text{Cl}_2$, respectively. In the case of SO_2 and CO , combination occurs only when the mixed gas is exposed to light or a catalyst such as charcoal.

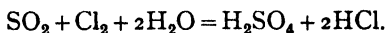
A solution of chlorine in water (chlorine water), which has a greenish-yellow colour and smells strongly of the gas, possesses strong bleaching and oxidising properties. It precipitates sulphur from a solution of hydrogen sulphide :



liberates iodine from a solution of potassium iodide :



and oxidises a solution of sulphur dioxide (sulphurous acid) to sulphuric acid :



When chlorine is passed into water cooled in ice an almost white crystalline solid chlorine hydrate $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ separates. On gentle heating the crystals melt with effervescence and pure chlorine is evolved.

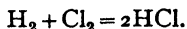
Atomic chlorine is said to be formed by the action of a high-tension electrodeless discharge on chlorine. It reacts with hydrogen in the dark.

HYDROGEN CHLORIDE (HYDROCHLORIC ACID)

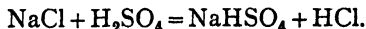
History.—See p. 147.

Occurrence.—Hydrogen chloride is found in some volcanic gases and in solution in some rivers in volcanic districts. Small quantities of free hydrochloric acid occur in human and animal gastric juice.

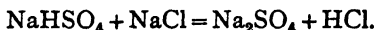
Preparation.—Hydrogen chloride is formed by the combustion of hydrogen in chlorine, and by the explosion of a mixture of the two gases when kindled, or exposed to light :



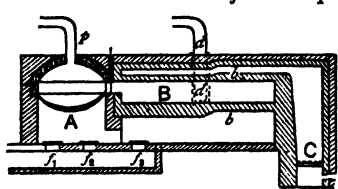
It is usually prepared by the action of concentrated sulphuric acid on common salt :



Only NaHSO_4 , sodium hydrogen sulphate or sodium bisulphate, is formed unless the temperature is higher than can be attained in a glass flask. This salt when *strongly* heated with common salt forms hydrochloric acid and normal sodium sulphate :



In the *laboratory preparation* common salt (sometimes rock salt or salt which has been fused is used) is placed in a fairly large flask (to allow space for frothing) and concentrated sulphuric acid added through a thistle funnel. Some gas is evolved at once but when the reaction slackens the flask is gently heated on wire gauze. The gas is collected in dry jars by downward displacement, as it is slightly heavier than air. When the jar is filled with gas copious white fumes issue from the mouth. These are formed by atmospheric moisture producing a mist of small



droplets of concentrated hydrochloric acid ; the dry gas is quite transparent and it does not fume with *dry* air. The gas may be dried by concentrated sulphuric acid or calcium chloride and collected over mercury.

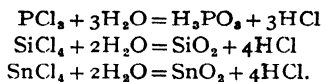
FIG. 89.—Salt-cake muffle furnace.

On the technical scale the reaction is carried out in a *salt-cake furnace* (Fig. 89) containing an iron pan A for the first stage of the process with formation of NaHSO_4 , and a hearth or fire-clay box (*muffle*) B, into which the pasty mass from the pan is raked and is strongly heated by the flames

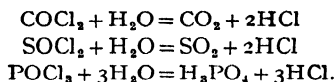
from the producer C to form Na_2SO_4 (*salt cake*). The gas is absorbed by water trickling over coke in a large brickwork or stone tower to form a crude solution of hydrochloric acid called *spirit of salt* or *muratic acid*, which is yellow on account of impurities (*e.g.* iron salts). This acid is transported in large globular glass bottles called *carboys* packed with straw into iron crates, or in large stoppered bottles called *Winchester quarts*. The acid is used for cleaning metals (*e.g.* iron sheets before galvanising) and other purposes.

Many other chlorides of metals (*e.g.* potassium, ammonium, calcium, aluminium, iron, etc.) evolve hydrogen chloride with concentrated sulphuric acid; lead, cuprous, silver and mercurous chlorides react more slowly, and mercuric chloride not at all.

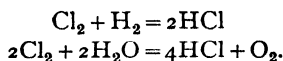
Hydrogen chloride is also evolved by the action of water on the chlorides of many non-metals (arsenic, boron, phosphorus, silicon and sulphur, but not nitrogen or carbon) and on stannic chloride:



Carbon, sulphur and phosphorus oxychlorides are also decomposed by water:



Synthetic hydrochloric acid is made from electrolytic chlorine (p. 152) by burning the chlorine in electrolytic hydrogen in silica tubes, and dissolving in distilled water; in another process chlorine and steam are passed over heated active charcoal as a catalyst:



Properties.—Hydrogen chloride is a colourless gas with a very pungent irritating odour, and attacks the mucous membranes of the nose and throat. It is not combustible and is a non-supporter of combustion. It is liquefied with difficulty. The gas and its concentrated solution fume in moist air, and form dense white fumes of ammonium chloride when brought in contact with ammonia gas:



The gas is very soluble in water, forming a very acid solution. The great solubility may be demonstrated by the *fountain experiment*.

A large dry round-bottom flask is filled with the gas by displacement (some time is required to expel all the air) and fitted with a rubber stopper

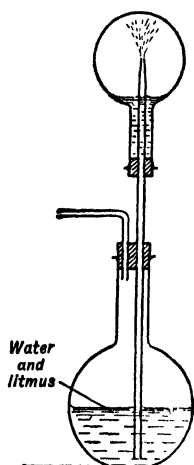
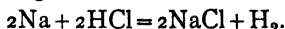


FIG. 90.—Fountain experiment.

carrying a tube drawn out into a jet. The flask is inverted with the tube dipping into water coloured with blue litmus contained in a second large flask, as shown in Fig. 90. By blowing into the short tube on the second flask a drop of water is forced into the upper flask. The gas is instantly dissolved, the water in the lower flask is driven in the form of a fountain into the upper flask, and the litmus is turned red by the acid solution formed.

When a *dilute* solution of hydrochloric acid is distilled weak acid passes over and the residue increases in concentration, with rise of boiling point. When the concentration reaches 20·2 per cent. the liquid distils with a constant composition and boiling point of 110°. This is called the *constant boiling solution*. Concentrated acid on distillation first loses hydrogen chloride gas with a little moisture, till the residue again reaches 20·2 per cent. and distils at 110°, this being the *maximum boiling point* of the acid. The constant boiling solution varies in composition with the pressure and hence it is not a true chemical compound.

Burning sodium continues to burn with a bright yellow flame in a jar of hydrogen chloride gas; if the plate of the deflagrating spoon is well greased the hydrogen formed in the jar may be kindled when the fume has settled. The gas is slowly decomposed by sodium amalgam:



Hydrogen chloride is only slightly dissociated by heat (*cf.* HI). Dry liquid hydrogen chloride does not act on zinc, iron, magnesium, quicklime and some carbonates, which dissolve in the aqueous acid.

Formula of hydrogen chloride.—The composition of hydrogen chloride may be determined either by *analysis* or by *synthesis*.

Analytical methods.—(i) Hydrochloric acid (sp. gr. 1·1) is electrolysed with gas carbon electrodes (Fig. 91), since platinum is attacked by chlorine. When the acid is saturated with chlorine, hydrogen and chlorine are evolved in equal volumes

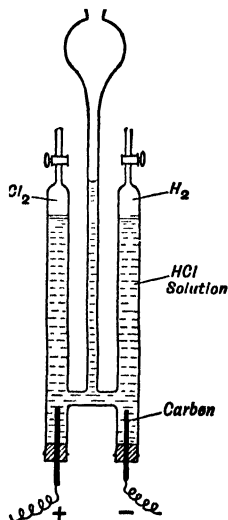


FIG. 91.—Electrolysis of hydrochloric acid.

(ii) The closed limb of the U-tube shown in Fig. 92 is filled with dry hydrogen chloride. The lower stopcock is closed and the mercury in the open limb is replaced by liquid sodium amalgam. This stopcock is then opened so as to bring the gas in contact with the amalgam, and the apparatus allowed to stand. A white crust of sodium chloride is slowly formed, and the volume of the gas after levelling is diminished to half. When mercury is poured into the open limb of the U-tube to displace the gas through the stopcock, it will be found to be inflammable and is hydrogen.

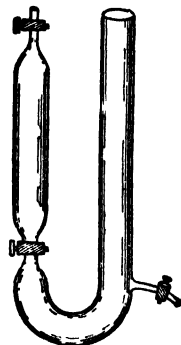


FIG. 92.—Decomposition of hydrogen chloride by sodium amalgam.

The experiment shows that 1 vol. of hydrogen chloride contains $\frac{1}{2}$ vol. of hydrogen, or 1 molecule of hydrogen chloride contains $\frac{1}{2}$ molecule or 1 atom of hydrogen. The formula is HCl_2 . The density of the gas gives the molecular weight 36.5. This contains 1 part of hydrogen, hence it contains 35.5 parts, or 1 atom, of chlorine and the formula is HCl .

Synthetic method.—The composition of hydrogen chloride may be shown by synthesis from hydrogen and chlorine.

(i) One half of a tube provided with stopcocks (Fig. 93) is filled with chlorine and the other half with hydrogen. The middle stopcock is



FIG. 93.—Synthesis of hydrogen chloride.

opened and the gases allowed to mix in a room with diffused daylight (in *sunlight* the gases combine with explosion). After a few hours combination is complete and the greenish colour of the chlorine disappears. One of the end stopcocks is opened under mercury and it is seen that there is no change in volume; if it is opened under water the latter dissolves the hydrogen chloride and fills the tube (provided that the hydrogen and chlorine were pure and that exactly equal volumes were used).

(ii) A mixture of equal volumes of hydrogen and chlorine is passed in the dark into the tube shown in Fig. 94, provided with platinum wires for

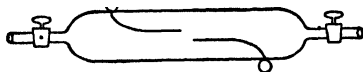


FIG. 94.—Explosion of a mixture of hydrogen and chlorine.

exploding the gas by a spark. *The tube is placed behind a strong glass screen* (in case it should burst) * and a spark is passed. There is a flash

* This has occurred in the author's experience.

of light in the tube and a click is heard. When the tube has cooled it is opened under mercury and water successively, with similar results to those described above.

These experiments show that :

1 vol. hydrogen + 1 vol. chlorine = 2 vols. hydrogen chloride.

Thus 2 molecules of hydrogen chloride contain 1 molecule of hydrogen and 1 molecule of chlorine, or 1 molecule of hydrogen chloride contains $\frac{1}{2}$ molecule (1 atom) of hydrogen and $\frac{1}{2}$ molecule (1 atom) of chlorine. Hence the formula is HCl. This may be *confirmed* by a measurement of the density of the gas.*

The atomic weight of chlorine was found as explained on p. 76.

* The student should note that the formula HCl is established in this case *without* a density determination. See Partington and Stratton, *Intermediate Chemical Calculations*, Chapter III.

CHAPTER XV

THE OXIDES AND OXYACIDS OF CHLORINE

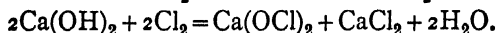
THE more important oxides and oxyacids of chlorine are summarised in the table below :

OXIDES		OXYACIDS	
Chlorine monoxide	Cl_2O	\longrightarrow	Hypochlorous acid HOCl
Chlorine dioxide - -	ClO_2		Chlorous acid HClO_2
			Chloric acid HClO_3
Chlorine heptoxide -	Cl_2O_7	\longrightarrow	Perchloric acid HClO_4

The oxides Cl_2O_3 and Cl_2O_5 corresponding with chlorous and chloric acids are unknown, but there is an oxide Cl_2O_6 . Chlorine dioxide dissolves without reaction in water, but it dissolves in *alkali hydroxide* solution to form salts of chlorous and chloric acids (p. 170), of which it may be regarded as a *mixed anhydride*.

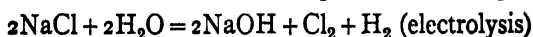
Hypochlorites.—When chlorine is passed into a cold solution of potassium or sodium hydroxide, so that excess of alkali remains, a liquid smelling like chlorine but with a difference is obtained. This liquid is more stable than chlorine water and was used under the name of *eau de Javelle* for bleaching. A similar bleaching liquid is formed when chlorine is passed into milk of lime.

These reactions form equimolecular amounts of hypochlorite and chloride:

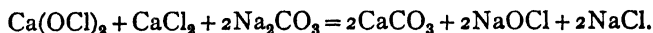


Hypochlorites were first obtained by Berthollet in 1786. The anhydride of hypochlorous acid HOCl , is chlorine monoxide Cl_2O , discovered by Balard in 1834.

Sodium hypochlorite solution containing sodium chloride is used as a disinfectant. It is prepared by the electrolysis of a solution of common salt so that the chlorine formed at the anode is allowed to react with the sodium hydroxide formed at the cathode (p. 152) and the liquid is kept cool :



It can also be prepared by mixing a solution of bleaching powder with sodium carbonate solution and filtering :



Chlorine monoxide.—Chlorine monoxide is prepared by passing a slow stream of dry chlorine over yellow precipitated oxide of mercury, previously heated to $300^\circ\text{--}400^\circ$, contained in a cooled tube (Fig. 95). A

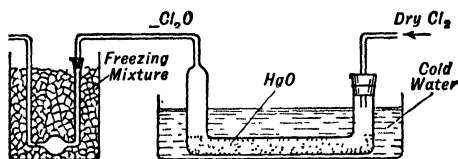


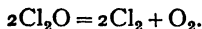
FIG. 95.—Preparation of chlorine monoxide.

brown oxychloride of mercury and brownish-yellow chlorine monoxide gas are formed :

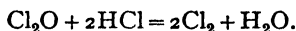


The chlorine monoxide is condensed to an orange-coloured liquid in a U-tube cooled in a freezing mixture. The gas may be collected by downward displacement as it attacks mercury (but only slowly) and is soluble in water.

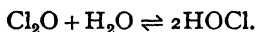
The gas explodes readily but not very violently on heating, giving a mixture of two volumes of chlorine and one volume of oxygen :



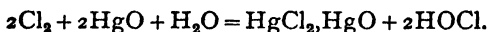
In this way its formula may be determined, the chlorine after explosion being absorbed by an alkali solution. Liquid chlorine monoxide may explode if the tube containing it is scratched with a file, but if quite free from organic matter it may be distilled without decomposition. Hydrogen chloride gas decomposes chlorine monoxide gas with production of chlorine :



The gas dissolves easily in water forming a pale golden-yellow solution containing **hypochlorous acid** :



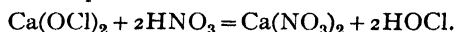
Hypochlorous acid is known only in solution. A solution of the acid is obtained by shaking chlorine water with yellow precipitated mercuric oxide and distilling :



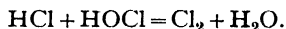
Hypochlorous acid is formed when a mixture of air and hydrogen chloride is bubbled through warm potassium permanganate solution :



Hypochlorous acid is best prepared from bleaching powder (p. 164). When dissolved in water this forms calcium chloride and hypochlorite. To a clear solution of bleaching powder the calculated amount of 5 per cent. nitric acid is added slowly from a burette whilst the liquid is kept well stirred, and the liquid is distilled :



Hydrochloric acid reacts with hypochlorous acid with liberation of free chlorine :



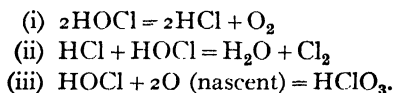
An excess of any acid capable of liberating hydrochloric acid from calcium chloride, when added to bleaching powder or its solution liberates *the whole* of the chlorine :



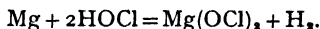
Care must therefore be taken not to add excess of nitric acid in the preparation of hypochlorous acid. Boric acid (which does not decompose the chloride) may be used, or carbon dioxide passed into bleaching powder solution :



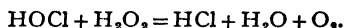
Hypochlorous acid in solution is pale golden yellow, or colourless when dilute. The dilute solution is fairly stable in the dark but concentrated solutions decompose on exposure to sunlight, with evolution of oxygen and chlorine and formation of some chloric acid :



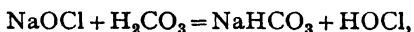
The acid dissolves magnesium with evolution of hydrogen :



Iron and aluminium evolve hydrogen and chlorine ; copper, nickel and cobalt evolve chlorine and oxygen. With hydrogen peroxide the acid and its salts evolve oxygen :

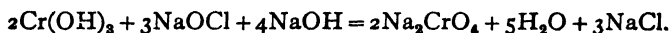


Hypochlorous acid is a very weak acid and even carbonic acid from atmospheric carbon dioxide liberates it from its salts :

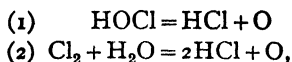


so that these have the smell of the free acid.

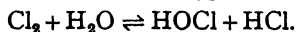
Hypochlorous acid and hypochlorites are *powerful oxidising agents* ; precipitated chromic hydroxide dissolves in alkaline sodium hypochlorite solution to form a yellow solution of sodium chromate :



The bleaching action of hypochlorous acid and that of chlorine water are probably due to nascent oxygen :

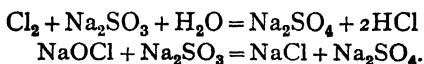


and chlorine water also contains some hypochlorous acid :

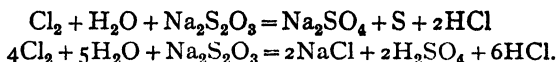


Equations (1) and (2) show that hypochlorous acid, for the same weight of chlorine, has twice the bleaching activity of free chlorine. There is no loss of bleaching activity when chlorine is first absorbed by alkali, although half is converted into inert chloride.

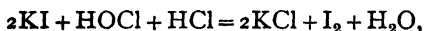
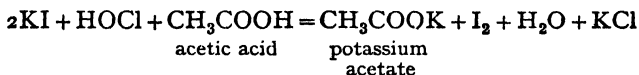
The chlorine, hypochlorous acid or hypochlorite is removed from the bleached material by washing and the last traces by washing with a solution of sodium sulphite or thiosulphate, which acts as an *antichlor* :



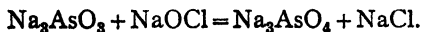
The reaction with thiosulphate is complicated :



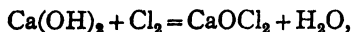
Hypochlorous acid and hypochlorites liberate iodine from potassium iodide :



and oxidise sodium arsenite solution to sodium arsenate :



Bleaching powder.—Chlorine gas does not react with *quicklime* at the ordinary temperature, but at a red heat oxygen is evolved and calcium chloride formed : $2\text{CaO} + 2\text{Cl}_2 = 2\text{CaCl}_2 + \text{O}_2$. If chlorine is passed over *slaked lime* it is rapidly absorbed, forming *bleaching powder* or *chloride of lime*, which smells of hypochlorous acid. The reaction is :



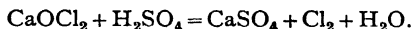
the water formed mostly remaining in the powder.

In the manufacture of bleaching powder the slaked lime is spread over the floors of closed lead chambers so as to expose a large surface and somewhat diluted chlorine gas admitted. At first the chlorine is rapidly absorbed but the reaction afterwards slows down. The powder is turned over with wooden rakes and the action of the gas continued until absorption is complete, which takes 12–14 hours. In modern works large rotating

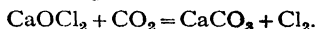
inclined iron cylinders cooled externally by water where the reaction is vigorous are used, the slaked lime passing down in the opposite direction to the chlorine diluted with air.

Good bleaching powder contains about 35 to 37 per cent. of *available chlorine*, i.e. chlorine liberated by acids and corresponding with CaOCl_2 . Some calcium hydroxide is always present.

It should be noted that the *whole* of the chlorine of CaOCl_2 is set free by acid :

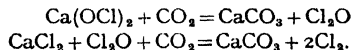


Moist carbon dioxide liberates a large proportion of the chlorine of bleaching powder on warming :



Formula of bleaching powder.—Bleaching powder was at first regarded as a molecular compound of lime and chlorine, "chloride of lime" CaO, Cl_2 . Balard in 1835 suggested that it was a *mixture* of equimolecular amounts of calcium hypochlorite and chloride : $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2$. This does not agree with the facts : (1) good bleaching powder is not nearly so deliquescent as calcium chloride ; (2) alcohol extracts very little calcium chloride from good dry bleaching powder although it readily dissolves calcium chloride ; (3) according to Lunge nearly 90 per cent. of the total chlorine of bleaching powder is liberated at 70° by damp carbon dioxide, which has no action on calcium chloride.

The liberation of chlorine by carbon dioxide could be explained by the action of chlorine monoxide, set free from the hypochlorite, on calcium chloride in presence of carbon dioxide :



The failure to extract calcium chloride by alcohol from bleaching powder could be explained if it existed as a basic chloride, $\text{CaCl}_2, \text{Ca}(\text{OH})_2$, which is non-deliquescent and insoluble in alcohol.

Stahlschmidt suggested that bleaching powder contains a basic hypochlorite, $\text{Ca}(\text{OH})(\text{OCl})$, and Odling (1861) that it is a chloro-hypochlorite, $\text{Ca}(\text{OCl})\text{Cl}$, hypothetically formed from hypochlorous and hydrochloric acids and calcium hydroxide :



O'Shea (1883) * decided between the three rival formulae of Balard, Stahlschmidt and Odling as follows.

He removed any free calcium chloride by treatment with alcohol and determined in the residue : (i) the total lime CaO ; (ii) the total chlorine ;

* *J. Chem. Soc.*, 1883, 43, 410.

(iii) the chlorine as hypochlorite. Only Odling's formula agreed with the results.

	<i>Residue</i>	CaO	CaO	<i>hypochlorite Cl</i>
		<i>total Cl</i>	<i>hypochlorite Cl</i>	<i>total Cl</i>
1. Balard -	- Ca(OCl) ₂	1 : 2	1 : 2	1 : 1
2. Stahlschmidt -	Ca(OH)OCl	1 : 1	1 : 1	1 : 1
3. Odling -	- Ca(OCl)Cl	1 : 2	1 : 1	1 : 2
4. Found -	- - -	1 : 2	1 : 1	1 : 2

Ordinary bleaching powder always contains some calcium hydroxide, apparently in a combined form, and Neumann and Hauck (1926) supposed that normal bleaching powder is the compound $3\text{Ca}(\text{OCl})\text{Cl}, \text{Ca}(\text{OH})_2, 5\text{H}_2\text{O}$, the active constituent being Odling's compound $\text{Ca}(\text{OCl})\text{Cl}$. In complete absence of moisture a very hygroscopic compound $3\text{Ca}(\text{OCl})\text{Cl}, \text{Ca}(\text{OH})_2, 3\text{H}_2\text{O}$ was formed, and at low temperatures $\text{Ca}(\text{OCl})\text{Cl}, \text{Ca}(\text{OH})_2, \text{H}_2\text{O}$ was obtained.

Bunn, Clark, and Clifford (*Proc. Roy. Soc.*, 1935, 151, 141), on the basis of chemical and microscopic evidence, proposed a different view of the constitution of bleaching powder. The first products of the action of chlorine on slaked lime are basic calcium hypochlorite $\text{Ca}(\text{OCl})_2, 2\text{Ca}(\text{OH})_2$, and a non-deliquescent basic calcium chloride $\text{CaCl}_2, \text{Ca}(\text{OH})_2, \text{H}_2\text{O}$. On further chlorination, the basic hypochlorite tends to pass into crystalline calcium hypochlorite $\text{Ca}(\text{OCl})_2, 4\text{H}_2\text{O}$, recognised microscopically, and ordinary bleaching powder is regarded as a mixture of this and basic calcium chloride. For many purposes, the old formula CaOCl_2 can be used, but it seems as if bleaching powder is not a single chemical substance but a mixture.

A solution of sodium hypochlorite is sometimes used for bleaching purposes instead of bleaching powder, and then contains 1 to 2 per cent. of NaOCl. A crystalline hydrate $\text{NaOCl}, 5\text{H}_2\text{O}$ is known.

Calcium hypochlorite $\text{Ca}(\text{OCl})_2$ is prepared in crystals by passing chlorine into milk of lime and evaporating the clear solution *in vacuo*. The crystalline hydrate $\text{Ca}(\text{OCl})_2, 4\text{H}_2\text{O}$ is first deposited on evaporation. The commercial product (*maxochlor*) is more stable than bleaching powder and is completely soluble in water.

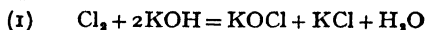
Chlorates.—When chlorine is passed into a solution of potassium or sodium hydroxide, only hypochlorite and chloride are formed as long as the liquid remains alkaline, and the solution may be boiled without much change. As soon as the chlorine is in excess the hypochlorite is rapidly converted into chlorate and chloride, with evolution of heat. The *total* reaction is :



Probably free hypochlorous acid is involved as an intermediate stage :



and oxidises the hypochlorite :



If we multiply (1) by 3 and (3) by 2 and add the three equations we obtain the usual equation for the whole reaction.

Chlorine generated from manganese dioxide and hydrochloric acid is washed with a little water and passed into potassium hydroxide solution (20 gm. of KOH in 40 c.c. of water) in a beaker. Crystals separate and to prevent the delivery tube becoming choked an inverted funnel is used. When the liquid smells strongly of chlorine it is cooled and decanted from the crystals of chlorate, which are washed once or twice with a little cold water and then recrystallised from hot water.

Potassium chlorate was discovered by Berthollet in 1786. It gives certain reactions characteristic of all chlorates :

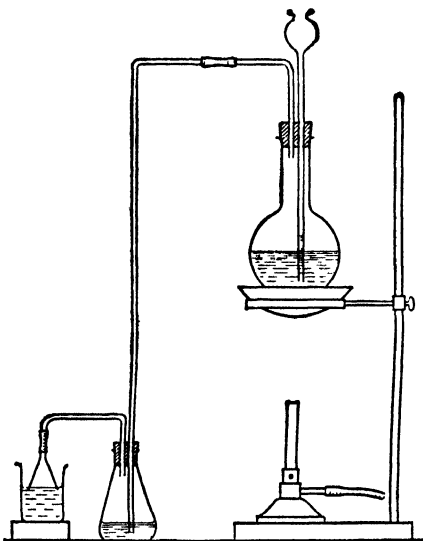


FIG. 96.—Preparation of potassium chlorate.

(1) Solutions give no precipitate with silver nitrate but the dry salt, on heating, gives off oxygen and the residue of chloride when dissolved in water gives a white precipitate of silver chloride with silver nitrate and dilute nitric acid.

(2) If a solution of potassium chlorate is mixed with indigo solution and a few drops of sodium sulphite solution, the colour is discharged. The chlorate is reduced by the sulphurous acid to a lower oxide of chlorine with strong bleaching properties.

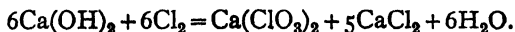
(3) A crystal of potassium chlorate with three drops of concentrated sulphuric acid in a test-tube turns orange-yellow and evolves a yellow explosive gas (chlorine dioxide ClO_2) having a peculiar odour. On warming there is a crackling noise due to explosions of the ClO_2 . (Care must be taken, as some acid is often thrown out of the tube.)

(4) Potassium chlorate warmed with concentrated hydrochloric acid

gives off a yellow explosive gas (*euchlorine*) which is a mixture of chlorine and chlorine dioxide: $8\text{KClO}_3 + 24\text{HCl} = 8\text{KCl} + 12\text{H}_2\text{O} + 9\text{Cl}_2 + 6\text{ClO}_2$.*

Potassium chlorate detonates violently when triturated with phosphorus or sulphur (*dangerous*). A mixture of the chlorate and sulphur detonates on percussion.

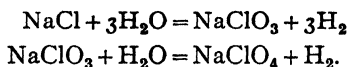
Chlorates are manufactured by the action of excess of chlorine on concentrated solutions of alkalis or by electrolysis. Calcium chlorate is made by passing chlorine into hot milk of lime in cast-iron vats with agitating paddles until the reaction is complete:



On adding potassium chloride the sparingly soluble potassium chlorate crystallises and is recrystallised. It is usual to make the very soluble sodium chlorate. The solution of calcium salts is concentrated, cooled and filtered from the crystals of hydrated calcium chloride which separate. Excess of sodium sulphate is added, when all the calcium is precipitated as sulphate. On evaporation of the filtered solution sodium chloride separates, which is removed and on cooling sodium chlorate crystallises.

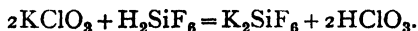
Chlorate and perchlorate are also made by the electrolysis of hot saturated sodium chloride solution between platinum electrodes placed close together. A little potassium dichromate is added. The chloride is first completely converted into *chlorate* and on prolonged electrolysis this passes into *perchlorate*.

The total reactions are:

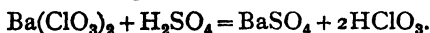


Chlorates are used as oxidising agents (*e.g.* in the oxidation of aniline to aniline black), potassium chlorate is used in making matches and fire-works, and sodium chlorate as a weed-killer. Perchlorates are used in the manufacture of detonators and explosives.

Chloric acid.—If a solution of potassium chlorate is precipitated with hydrofluosilicic acid, sparingly soluble potassium silicofluoride is formed and the chloric acid solution can be filtered off:



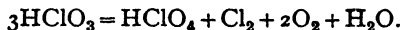
It is more convenient to use barium chlorate, a solution of which is precipitated with diluted sulphuric acid:



The excess of sulphuric acid is precipitated with baryta water, the solution is decanted and is evaporated in a vacuum desiccator over

* This is the usual equation as the gas is said to give a mixture of 2 vols. of chlorine and 1 vol. of oxygen when decomposed by heat.

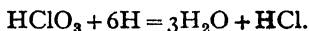
concentrated sulphuric acid until it contains 40 per cent. of HClO_3 . On further concentration the acid decomposes into chlorine, oxygen and perchloric acid :



Chloric acid was first prepared from barium chlorate by Gay-Lussac in 1814.

Concentrated chloric acid is colourless and fairly stable in the dark ; it is more stable than hypochlorous acid. When exposed to light it undergoes decomposition and becomes yellow. Organic substances such as cotton wool or paper are ignited by the concentrated acid. It has a pungent smell rather like that of ozone and has strong oxidising and bleaching properties. Unlike hypochlorous acid, it is a strong acid.

Chloric acid evolves hydrogen with zinc but in acid solutions chlorates are readily reduced by iron or aluminium powder to hydrochloric acid (perchloric acid is not reduced in dilute solution) :

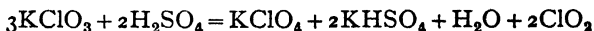


The structural formula of chloric acid is $\text{H}-\text{O}-\overset{\text{v}}{\underset{\text{O}}{\text{Cl}}}=\overset{\text{O}}{\text{O}}.$

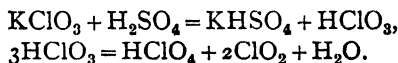
Chlorine dioxide.—Thos. Hoyle in 1797 obtained a yellow explosive gas from potassium chlorate and concentrated sulphuric acid but did not recognise it as an oxide of chlorine. Davy in 1815 showed that it was chlorine dioxide. On explosion, two volumes gave three volumes of a mixture of two volumes of oxygen and one volume of chlorine (absorbed by alkali) : $2\text{ClO}_2 = \text{Cl}_2 + 2\text{O}_2$. The density of chlorine dioxide (sometimes called chlorine peroxide) gas was found by Pebal and Schacherl in 1882 to correspond with ClO_2 .

Powdered previously fused potassium chlorate is added in small quantities at a time to cooled concentrated sulphuric acid in a small retort. The orange-yellow paste is very cautiously warmed by placing the retort in lukewarm water, and the gas collected by downward displacement. It dissolves in water and attacks mercury. *There is considerable danger of violent explosion in the preparation of chlorine dioxide and no attempt should be made by the student to prepare it by this method.*

The reaction * is :



and appears to take place as follows :



* This equation seems to offer peculiar difficulty to some students.

When passed through a tube cooled in a freezing mixture the gas condenses to a dark-red liquid, which freezes when strongly cooled to an orange-coloured crystalline solid. The liquid and solid are slowly decomposed by exposure to light. The liquid is violently explosive, although it may be distilled without decomposition in the entire absence of organic matter. The gas also explodes readily in contact with a hot glass rod, by an electric spark, and in contact with turpentine, alcohol or ether. Chlorine dioxide is a powerful oxidising agent.

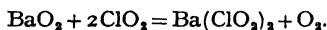
Equal parts of powdered sugar or starch and potassium chlorate are mixed with a spatula on a sand bath and a drop of concentrated sulphuric acid is put on the mixture from a glass rod. The mass ignites and burns violently.

A little potassium chlorate is placed in a glass of water and one or two small fragments of phosphorus thrown in. A few c.c. of concentrated sulphuric acid are *carefully* poured down a thistle funnel on to the chlorate ; there is a series of flashes of light accompanied by harmless explosions—unless too much acid is added at once.

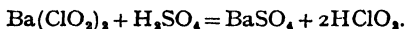
Chlorous acid.—Chlorine dioxide dissolves unchanged in water to form a yellow solution, but on adding an *alkali* a mixture of a chlorite and chlorate is formed :



Since the salts are difficult to separate it is better to use sodium or barium peroxide instead of alkali, when only chlorite is formed :

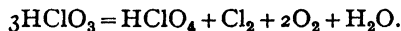


A solution of **chlorous acid** is obtained by precipitating a solution of barium chlorite with dilute sulphuric acid :



It is unstable and is an oxidising agent.

Perchloric acid.—Potassium perchlorate and perchloric acid were discovered by Stadion in 1816, but pure perchloric acid was first obtained by Roscoe in 1863. \ Small quantities of sodium perchlorate NaClO_4 occur in crude Chile nitre ; unlike the potassium salt it is very soluble in water. Perchloric acid is formed by the decomposition of chloric acid, especially on distillation :



Potassium perchlorate is formed on heating the chlorate (p. 107) :



About 25 gm. of *pure* potassium chlorate is heated in a *new* porcelain dish until the fused salt becomes pasty. The cold mass is ground in a mortar with cold water and washed with a little cold water. The residue is boiled with a little concentrated hydrochloric acid to decompose

any chlorate, diluted, filtered and washed twice with cold water. On re-crystallising from hot water potassium perchlorate is obtained. A better yield is obtained if a silica dish is used.

Potassium perchlorate gives the following reactions :

(1) It decomposes at a higher temperature than the chlorate :

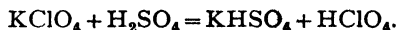


(2) It does not bleach indigo in presence of sulphites.

(3) With concentrated sulphuric acid it does not give a yellow explosive gas but dense white fumes of perchloric acid.

(4) It does not act upon hydrochloric acid.

If potassium perchlorate is distilled with four times its weight of very concentrated sulphuric acid in a small retort, perchloric acid comes over as a colourless or slightly yellow strongly fuming liquid :



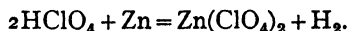
The yield is increased by carrying out the distillation under reduced pressure.

During the distillation under ordinary pressure, the liquid in the receiver gradually solidifies to white crystals of the stable monohydrate, $\text{HClO}_4 \cdot \text{H}_2\text{O}$. Other crystalline hydrates are known.

Anhydrous perchloric acid is a very dangerous substance which explodes violently when suddenly heated and sometimes spontaneously on keeping, when it undergoes decomposition. It is very hygroscopic and dissolves in water with a hissing noise and great evolution of heat. Paper and wood catch fire when the anhydrous acid is dropped on them. If a few drops of the acid are poured on recently-ignited wood charcoal there is a violent explosion.

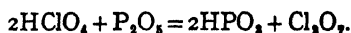
The aqueous acid, which is quite stable, is conveniently prepared by adding ammonium perchlorate (a commercial substance) dissolved in concentrated hydrochloric acid to warm concentrated nitric acid in a porcelain dish. A complicated reaction takes place, and on evaporation aqueous perchloric acid remains: it may be distilled at 200 mm. pressure.

The aqueous acid dissolves iron and zinc to form perchlorates and the acid is not reduced by nascent hydrogen (*cf.* HClO_3) :

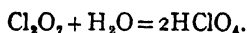


It is reduced by titanium trichloride TiCl_3 , or in alkaline solution by ferrous hydroxide. It is a much less powerful oxidising agent than chloric acid. Perchloric acid is a strong acid.

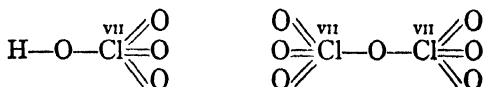
Chlorine heptoxide Cl_2O_7 is the anhydride of perchloric acid and is made by dehydrating anhydrous perchloric acid with phosphorus pentoxide and carefully distilling :



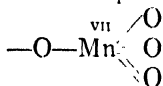
It is a colourless explosive liquid which decomposes on standing. It is more stable than chlorine dioxide and may be poured on paper, sulphur or even phosphorus without explosion, but detonates when heated or struck. With water it slowly forms perchloric acid :



The structural formulae of perchloric acid and chlorine heptoxide are :



Manganese occurs in the same group in the Periodic Table as chlorine and is assumed to be 7-valent in the permanganate radical :



and potassium permanganate KMnO_4 is isomorphous with potassium perchlorate KClO_4 .

CHAPTER XVI

FLUORINE, BROMINE AND IODINE

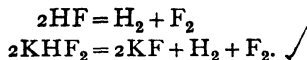
FLUORINE

History.—Fluorspar or *fluorite* (native calcium fluoride CaF_2) occurs in Derbyshire and other places in cubic crystals sometimes coloured blue ("Blue-John"), and is mentioned by Agricola (1530). Hydrofluoric acid was known about 1720. Scheele in 1771 discovered silicon fluoride SiF_4 . Although Davy in 1813 recognised that fluorine is an element analogous to chlorine, he was unable to isolate it and this was first accomplished by Moissan in 1886.

The atomic weight of fluorine, however, was determined in 1818 by Berzelius from the reaction $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$.

Occurrence.—Fluorine occurs as fluorspar and other fluorides. The mineral *cryolite*, a double fluoride of sodium and aluminium $\text{AlF}_3 \cdot 3\text{NaF}$ or Na_3AlF_6 , is found in Greenland, and *fluor-apatite* $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, is common. Small quantities of calcium fluoride in the soil, probably derived from apatite, are absorbed by plants, the ashes of which contain traces of fluoride. From plants calcium fluoride passes into the bones and teeth of animals, especially into the enamel of teeth. Traces of fluorides in drinking water, however, act very injuriously on the teeth.

Preparation.—Fluorine is always made by the electrolysis of anhydrous hydrofluoric acid or an acid fluoride :



Moissan found that anhydrous hydrofluoric acid does not conduct an electric current, but becomes conducting when potassium hydrogen fluoride KHF_2 is dissolved in it.

This solution is electrolysed in a U-tube of an alloy of platinum and iridium with electrodes of the same material, the whole being strongly cooled. Hydrogen is evolved from the cathode and fluorine from the anode. Moissan later found that the U-tube could be of copper, which apparently becomes coated with a protecting film of fluoride, but the electrodes must still be of platinum-iridium.

The electrodes are insulated by fluorspar stoppers covered outside with shellac. The tube is cooled in a bath of methyl chloride (b. pt. -23°) (Fig. 97). The fluorine is passed through a platinum or copper spiral

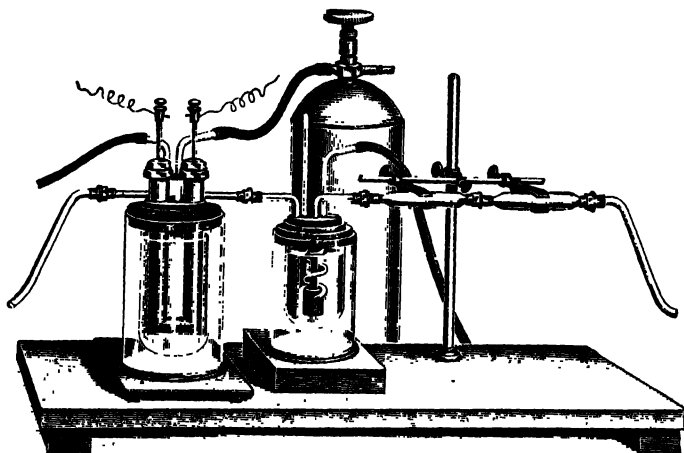


FIG. 97.—Moissan's apparatus for preparing fluorine.

cooled in methyl chloride and a tube of the same metal packed with fused sodium fluoride, to remove hydrofluoric acid vapour. By collecting and measuring the hydrogen from the cathode and absorbing the fluorine in iron wire in a weighed platinum tube, Moissan found that for every gram of hydrogen evolved the iron increased in weight by 19 grams. The gas was therefore free fluorine.

Fluorine is more easily prepared by the electrolysis of fused KHF_2 in a copper vessel *AA* (Fig. 98) with graphite electrodes *RR*. A magnesium vessel can also be used. The salt must be very pure and dry and the electrodes of pure carbon. A current of 5 amps. at 12 volts is used. The fluorine evolved is purified by passing it through two copper U-tubes *FG* containing dry sodium fluoride.

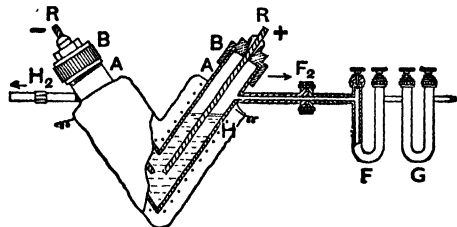


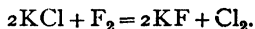
FIG. 98.—Preparation of fluorine.

The working temperature is about 105° . The cell is a rectangular steel tank, the cathodes are of steel and the anodes of amorphous carbon. Currents up to 2000 amp. are used. Fluorine gas is available compressed in steel cylinders.

Properties.—Fluorine is a pale greenish-yellow gas with very little action on glass. It has a powerful odour resembling hypochlorous acid, but is not so poisonous as hydrofluoric acid vapour. By weighing the gas in a glass flask Moissan found the density 19 ($H=1$), hence the formula is F_2 . Fluorine was liquefied in 1897 by Moissan and Dewar, who cooled the gas in liquid air boiling in a vacuum. It forms a clear yellow liquid and by cooling in liquid hydrogen Dewar (1903) obtained pale yellow solid fluorine.

Fluorine fumes in moist air. It is the most active element known; it does not react directly with oxygen or nitrogen although compounds are formed indirectly, and it combines with chlorine only on heating, forming ClF and ClF_3 .

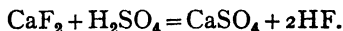
It unites explosively with moist hydrogen in the dark; sulphur, phosphorus, bromine, iodine, arsenic, antimony, silicon, boron, carbon, and potassium all ignite spontaneously in the gas and burn with the formation of fluorides. A jet of fluorine ignites at once in a jar of hydrogen, burning with a red-bordered flame and producing HF , which attacks the glass. Iron, zinc, tin, magnesium and silver take fire when gently warmed. Lead is only slowly attacked at the ordinary temperature, and copper and mercury become coated with a protective layer of fluorides. Gold and platinum are not attacked at the ordinary temperature but are corroded and form fluorides on heating. Alcohol, ether and turpentine take fire spontaneously in the gas. Potassium chloride is decomposed with evolution of chlorine:



Fluorine was said to react with water to form ozonised oxygen but it is possible that fluorine oxide is formed (p. 177). With bromine it forms BrF , BrF_3 and BrF_5 , and with iodine IF_3 and IF_5 .

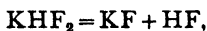
Hydrofluoric acid.—Hydrogen and fluorine combine with explosion in the dark, forming hydrogen fluoride or hydrofluoric acid. This is more conveniently obtained by the action of sulphuric acid on fluorides or by heating acid potassium fluoride.

Powdered fluorspar is distilled with 90 per cent. sulphuric acid in a lead retort connected with a lead receiver containing water; the vapour of hydrofluoric acid dissolves in the latter to form a colourless solution:

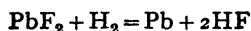


This is kept in wax or gutta-percha bottles.

Anhydrous hydrofluoric acid is made by distilling dry potassium hydrogen fluoride (*Fremy's salt*) in a platinum or copper retort with a condenser of the same metal cooled in a freezing mixture:



or by heating lead fluoride in hydrogen :

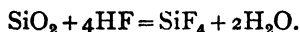


It must be kept in platinum or ceresin wax bottles

Anhydrous hydrofluoric acid is a colourless, strongly-fuming liquid, boiling at 19° ; it should therefore be kept in a freezing mixture. It does not solidify until strongly cooled. When quite free from water the liquid is said not to attack glass or metals at the ordinary temperature except potassium, which explodes in contact with it. According to Moissan the dry *gas* attacks glass. In the presence of traces of water the acid attacks glass violently and the aqueous acid attacks most metals (except gold, platinum, silver, mercury and lead) with evolution of hydrogen : $\text{Fe} + 2\text{HF} = \text{FeF}_2 + \text{H}_2$.

The acid and its vapour are dangerous corrosive poisons. They attack the skin violently and form sores which heal only with great difficulty.

Hydrofluoric acid and fluorides are antiseptics ; zinc and sodium fluorides are used in preserving wood. The acid is used for removing sand from castings and for etching glass. Hydrofluoric acid attacks silica, forming silicon fluoride :



Glass consists of sodium and calcium silicates ; these are decomposed with formation of fluorides and silicon fluoride (or if the aqueous acid is used hydrofluosilicic acid, p. 439) and the reaction is used as a test for fluorides.

A watch-glass is covered with melted beeswax and when cold a design is scratched through the wax by a needle. The glass is placed over a lead or platinum dish containing a mixture of powdered fluorspar and concentrated sulphuric acid, which may be gently warmed. On removing the wax with benzene the design is seen to be etched in the glass. If only traces are present, the design is seen by breathing on the glass.

Etchings made with the liquid acid are clear, those made with the gas are opaque.

The composition of hydrofluoric acid was determined by Gore (1869), who heated silver fluoride in hydrogen in a platinum vessel and obtained twice the volume of hydrofluoric acid gas. Hence the formula is HF_2 . The vapour density of the gas at 100° determined in a platinum flask corresponds with the molecular weight 20, hence the formula is HF , since the atomic weight of fluorine is 19 (Thorpe and Hambly, 1889). At lower temperatures the density shows that the gas contains more complex molecules, $(\text{HF})_n$.

The fluorides differ in many respects from the other halogen (p. 190) compounds. Silver fluoride is very soluble but calcium fluoride is nearly

insoluble in water, whilst silver chloride, bromide and iodide are insoluble and the calcium salts soluble.

Non-metal fluorides form complex compounds with hydrofluoric acid : *e.g.* HBF_4 , H_2SiF_6 , etc., which form salts, *e.g.* KBF_4 , K_2SiF_6 , etc.

Fluorine monoxide F_2O is a stable gas formed by bubbling fluorine slowly into dilute sodium hydroxide solution :



It is a powerful oxidising agent. Fluorine dioxide F_2O_2 is an orange-red solid formed by the action of an electric discharge on a mixture of fluorine and oxygen at low temperature and pressure. Above -100° it decomposes into fluorine and oxygen.

The atomic weight of fluorine has been found by converting calcium, sodium and potassium fluorides into the corresponding sulphates.

BROMINE

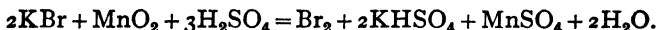
History.—Bromine was discovered by Balard in 1826 in the residues from the manufacture of salt from sea water. These liquors are known as *bittern* and contain magnesium bromide MgBr_2 . When treated with chlorine a yellow colour is produced due to liberation of free bromine :



Bromine was recognised as an element of the same character as chlorine and its discovery was further evidence in favour of the elementary nature of the latter. The free element is a dark-red heavy liquid giving a red vapour with a most irritating odour, hence its name (from the Greek, *bromos*, a stench).

Occurrence.—Bromine occurs in the rare mineral *bromargyrite* AgBr . Magnesium and alkali metal bromides occur in sea water, in some mineral springs, in the Dead Sea and the Great Salt Lake (Utah), and in the Stassfurt salt deposits. The ancient purple dye ("Purple of Tyre") is a bromine derivative of indigo. Most of the bromine made commercially is now obtained from sea water.

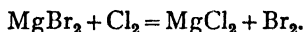
Preparation.—Bromine can be obtained by heating potassium bromide with diluted sulphuric acid and manganese dioxide in a retort :



It is better to condense the vapour under a little water in the receiver, as it is less likely to escape. The bromine separates out as a heavy dark-red liquid under a red layer of aqueous solution (bromine water). Bromine

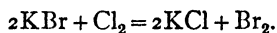
vapour attacks the eyes powerfully and the liquid has a corrosive action on the skin. The element is poisonous.

Bromine is prepared technically from the Stassfurt or Ohio bromides by passing chlorine and steam through a solution in a tower packed with pieces of porcelain (Fig. 99) :

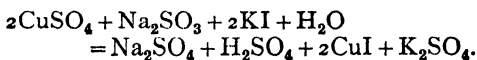


The bromine vapour is condensed by cooling and any passing on is caught by passing through moist iron filings, when a solution of iron bromides is formed, which is used in the preparation of potassium bromide (p. 182).

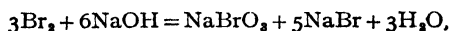
Bromine may be purified by careful distillation. Chlorine is removed by distillation over potassium bromide :



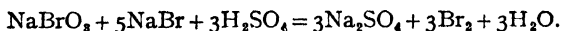
Iodine is removed as a precipitate of cuprous iodide by adding a solution of copper sulphate and sodium sulphite to a solution of impure potassium bromide :



Bromine is extracted in America (Wilmington N.C., etc.) from sea water which is acidified and chlorinated. The bromine vapour blown out by a current of air is absorbed in alkali and the mixture of bromate and bromide formed :



is acidified, when bromine is liberated (p. 183) :



To obtain 1 lb. of bromine 1800 gallons of sea water are treated. Most of the bromine is used in making ethylene dibromide ($\text{C}_2\text{H}_4 + \text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2$) for "ethyl petrol" containing lead tetraethyl. Some is used in making dyes, in gold extraction and in making bromides for medicinal use.

Properties.—Bromine is a heavy dark-red (almost black) liquid, boiling at 60° and giving off a red vapour at the ordinary temperature. The liquid explodes in contact with white phosphorus but red phosphorus burns forming phosphorus tribromide PBr_3 and pentabromide PBr_5 . Bromine also explodes in contact with potassium but does not act on sodium in the cold.

Bromine is somewhat soluble in water, forming a red solution (*bromine water*), and forms a solid hydrate $\text{Br}_2 \cdot 8\text{H}_2\text{O}$ on cooling in presence of

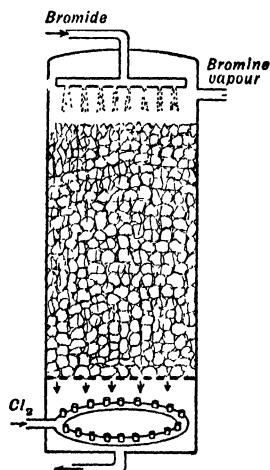
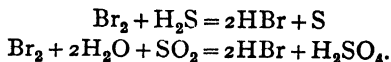


FIG. 99.—Technical preparation of bromine.

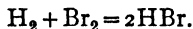
water. Bromine water has a feeble bleaching action, it turns starch paste yellow, and possesses oxidising properties.

In most of its chemical properties bromine resembles chlorine but is less energetic. It is an oxidising agent :

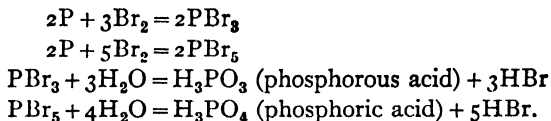


Both these reactions occur in solution.

Hydrogen bromide.—Hydrogen and bromine vapour do not combine readily but when the mixture is passed over heated platinum (a catalyst) gaseous hydrogen bromide (hydrobromic acid) formed :



Another method of preparation is to drop bromine *cautiously* on a paste of *red* phosphorus and water in a flask and pass the gas over moist red phosphorus in a U-tube to remove bromine vapour. The gas is collected by downward displacement (Fig. 100). Phosphorus tribromide and pentabromide are first formed and then decomposed by water :



The gas may be dried with calcium chloride or phosphorus pentoxide and collected over mercury.

The method of heating a salt with concentrated sulphuric acid which was used for the preparation of hydrochloric acid (p. 156) is not suitable for the preparation of hydrobromic acid. This is first liberated but, unlike hydrochloric acid, it can act as a reducing agent. It reduces the hot concentrated sulphuric acid to sulphur dioxide and the hydrobromic acid evolved is mixed with sulphur dioxide and bromine vapour :

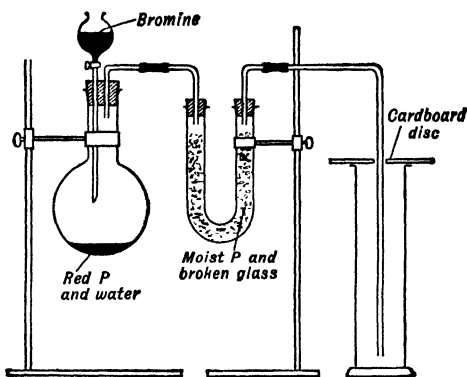
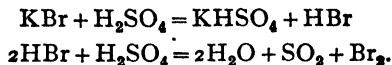
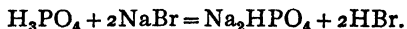


FIG. 100.—Preparation of hydrogen bromide.

When syrupy phosphoric acid is heated with the bromide, however, hydrobromic acid alone is evolved :



A solution of hydrobromic acid may be prepared by passing the gas into water with the apparatus shown in Fig. 101 in order that water may not be driven into the generating flask if the current of gas slackens. The saturated solution fumes strongly in moist air.

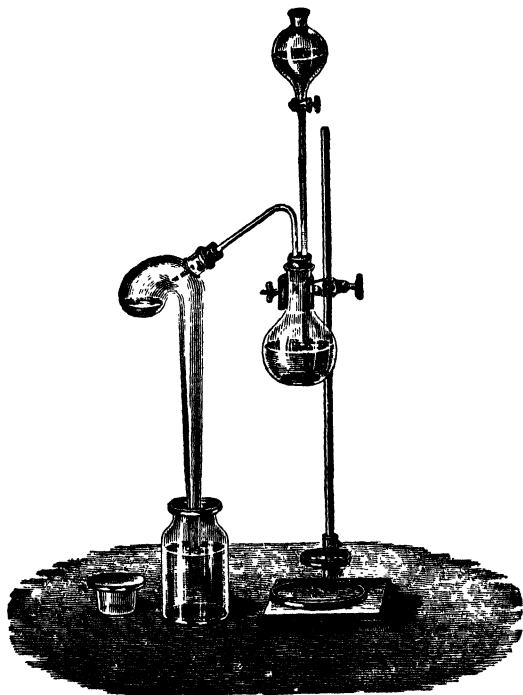
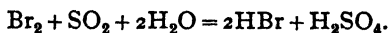
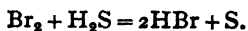


FIG. 101.—Preparation of hydrobromic acid solution.

A solution may also be prepared by passing sulphur dioxide into water covering a layer of bromine :

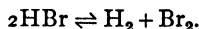


The liquid is then distilled, when a solution of hydrobromic acid of maximum boiling point (126° , 47.5 per cent. HBr) passes over. Hydrogen sulphide may be used instead of sulphur dioxide :

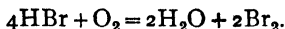


The solution of hydrobromic acid is filtered from the sulphur and distilled.

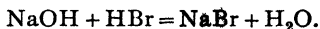
Hydrogen bromide is a colourless gas with an irritating acid smell ; it is heavier than air, fumes strongly in moist air, and is very readily soluble in water to form an acid solution. It may be condensed to a colourless liquid and a solid by strong cooling. The gas is less stable than hydrogen chloride and dissociates slightly when strongly heated :



The solution oxidises slowly when exposed to air and light and becomes yellow from liberation of bromine :



Aqueous hydrobromic acid dissolves metals (even copper, with hot concentrated acid) with evolution of hydrogen, and reacts with oxides, hydroxides or carbonates to form *bromides* :



The formula of hydrogen bromide may be determined by decomposing the gas with sodium amalgam (p. 159), when half the volume of hydrogen remains. Thus 1 molecule of the gas contains $\frac{1}{2}$ molecule (or 1 atom) of hydrogen and the formula is HBr_2 . The density shows that the molecular weight is 81, hence the molecule contains 80 parts or 1 atom of bromine and the formula is HBr . Since the density of bromine vapour shows that the molecular weight is $2 \times 80 = 160$, it follows from the above that 1 vol. of bromine vapour ($\text{Br}_2 = 160$) combines with 1 vol. of hydrogen ($\text{H}_2 = 2$) to form 2 vols. of hydrogen bromide ($\text{HBr} = 81$).

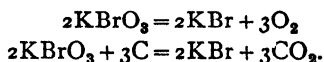
Bromides.—Bromides are obtained from bromine on the technical scale. It is important to remember, however, that neither bromides nor iodides (*q.v.*) can be obtained *directly* in the pure state by the action of the element on alkali hydroxides. The action is similar to that of chlorine : in the cold with excess of alkali an unstable hypobromite and a bromide are formed :



whilst in hot concentrated solution with excess of a bromine, a bromate and a bromide are produced :

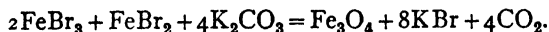


The mixture of bromide and bromate is evaporated to dryness and the residue heated alone or better with powdered charcoal (when the bromate is decomposed at a lower temperature) :

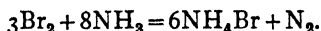


The mass is dissolved in water, filtered from excess of charcoal, evaporated and crystallised.

Another method is to shake iron filings with water and bromine, when a solution of bromides of iron is formed. This is treated with potassium carbonate and the black hydrated ferrosferric oxide filtered off :



Ammonium bromide free from bromate is obtained by the action of bromine on ammonia solution :

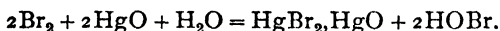


Bromides give with silver nitrate a *pale-yellow* precipitate of silver bromide AgBr, insoluble in dilute nitric acid and only sparingly soluble in dilute ammonia (white AgCl is soluble).

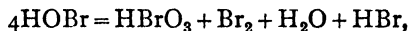
Nearly all bromides are soluble in water, cuprous, silver, lead and mercurous bromides being exceptions.

Oxides of bromine.—Unstable oxides of bromine Br_2O , BrO_2 and BrO_3 have been described ; the first is formed with mercuric oxide and bromine vapour (*cf.* Cl_2O) and the third from bromine vapour and ozone.

Hypobromous acid.—When bromine water is shaken with precipitated mercuric oxide a solution of hypobromous acid HOBr is formed :



The liquid may be distilled in a vacuum, when a solution of hypobromous acid is obtained. It is a straw-yellow liquid, decomposing when heated with production of bromine and bromic acid :

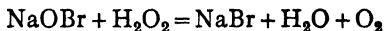


and is a powerful oxidising and bleaching agent.

If bromine is dissolved in cold aqueous alkali hydroxide an unstable hypobromite is formed :



These are used as oxidising agents and in the estimation of hydrogen peroxide and of urea, the oxygen and nitrogen evolved being measured (the carbon dioxide formed from urea dissolves in the alkaline hypobromite solution) :



On keeping, the hypobromite solutions decompose with formation of bromide and bromate :



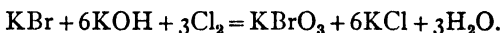
Bromine vapour is absorbed by dry slaked lime forming a red powder similar to bleaching powder. This probably contains CaOBr_2 ; when distilled with dilute nitric acid aqueous hypobromous acid passes over.

Bromic acid.—When bromine is dissolved in slight excess in hot concentrated alkali solution, a bromate and a bromide are obtained :

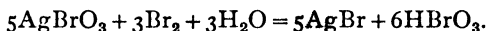


Potassium bromate is much less soluble than the bromide and the two salts may be separated by crystallisation, as in the case of the chlorate.

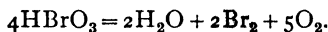
Potassium bromate is also formed by passing chlorine into an alkaline bromide solution :



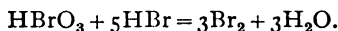
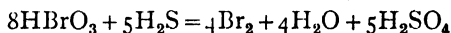
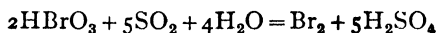
When silver nitrate is added to a solution of potassium bromate, white **silver bromate** AgBrO_3 is precipitated. When this is treated with bromine water, insoluble silver bromide is formed and the filtered solution contains **bromic acid** :



By concentration in a vacuum desiccator a 50 per cent. solution may be obtained, but more concentrated solutions give off bromine and oxygen :



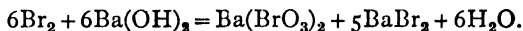
Bromic acid is a colourless liquid with a smell like dilute ozone, and is a powerful oxidising agent :



The bromates are usually sparingly soluble in water. On heating they decompose, evolving oxygen and sometimes bromine and leaving the bromide or oxide, or a mixture of both ; perbromates are not known.

Sodium bromate is made by the electrolytic oxidation of sodium bromide and its mixture with sodium bromide is called *bromine salt*, used in gold extraction.

Barium bromate $\text{Ba}(\text{BrO}_3)_2$ is precipitated when a slight excess of bromine is added to hot concentrated baryta water :



The bromide is soluble and remains in solution. If barium bromate is digested with dilute sulphuric acid and the excess of the latter removed by baryta water, the filtered solution contains bromic acid.

Chlorine merely dissolves in liquid bromine and no compound has been obtained in the pure state, although BrCl appears to exist to some extent in a mixture of chlorine and bromine vapour.

The **atomic weight of bromine** was determined from the ratios



also from the limiting density of hydrogen bromide.

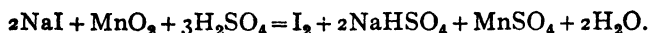
IODINE

History.—Iodine was discovered by Courtois in 1812 in the mother liquor from the manufacture of soda from kelp (burnt seaweed), but was first carefully investigated by Davy and by Gay-Lussac in 1813. They recognised that it was an element similar to chlorine. It was called iodine from the beautiful violet colour of the vapour (Greek, *ioeides*, violet). Davy discovered hydriodic acid, iodic acid and phosphonium iodide.

Occurrence.—Iodine occurs rather rarely as *iodargyrite* (silver iodide) and in some lead ores. Iodides occur in some mineral waters, *e.g.* of Woodhall Spa and Central Europe, and in sea water. Seaweeds and sponges extract iodine from sea water, and the ash of seaweed (called *kelp* or *varec*) contains iodides from which iodine is extracted. An important technical source of iodine is the small quantity of sodium iodate NaIO_3 present in *caliche*, the natural sodium nitrate of Chile.

Organic iodine compounds occur in cod-liver oil, milk, butter, green vegetables and especially in the thyroid gland. It is supposed to be essential to health and deficiency of iodine is said to produce the disease of goitre.

Preparation.—Iodine is prepared in the laboratory by heating a mixture of potassium (or sodium) iodide, manganese dioxide and diluted sulphuric acid in a retort :



Beautiful violet vapours are given off which condense in the cool neck of the retort and in the receiver as glittering black or grey scales of iodine.

On the technical scale iodine is prepared from *kelp*, which contains sodium and potassium iodides, chlorides, sulphates and carbonates, and some magnesium salts. The kelp is heated with water and the solution filtered and concentrated. The impurities largely crystallise out. The solution of iodides is then distilled with sulphuric acid and manganese dioxide in cast-iron retorts with lead covers, and the iodine which passes

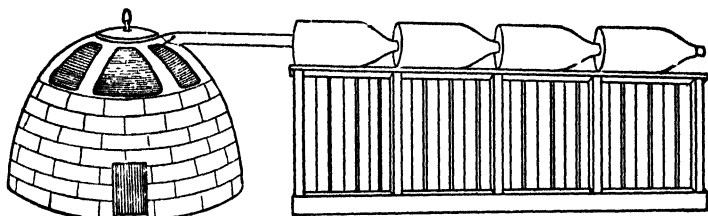
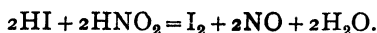


FIG. 102.—Technical preparation of iodine.

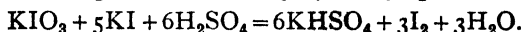
over is collected in stoneware receivers called *udells* (Fig. 102). It is washed with cold water, in which iodine is only slightly soluble, dried and sublimed, when it forms black steel-like glittering crystals. It may be

purified still further by resubliming it mixed with potassium iodide. In a more modern process the seaweed is not burnt but is extracted with sodium carbonate to remove iodide, and the residue can be used in preparing adhesives (*algin*).

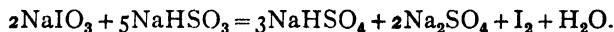
Iodine is prepared from salt springs in Java by precipitating as cuprous iodide (see p. 178), and from California brines from oil wells by acidifying and adding sodium nitrite :



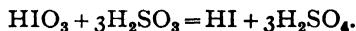
The iodine is adsorbed by charcoal from which it is dissolved by alkali and is set free by acidifying the solution of iodate and iodide formed :



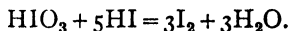
The preparation of iodine from iodides involves oxidation, that from iodates (*e.g.* from *caliche*) involves reduction. The mother liquor from the *caliche* contains sodium iodate. It is mixed with a solution of sodium hydrogen sulphite, and the iodine precipitated is filtered off, pressed, and sublimed :



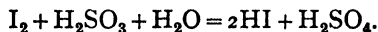
This reaction takes place in stages. The iodate (iodic acid) is reduced to iodide (hydriodic acid) by a rather slow reaction :



The hydriodic and iodic acids react rapidly as fast as produced to form iodine :



As long as any sulphite remains the iodine is reduced to hydriodic acid by a rapid reaction :



Iodine appears only when all the free sulphurous acid is used up, and the reaction has a period of induction. This is shown in Landolt's experiment.

Dissolve 1 gm. of crystallised iodic acid in 100 c.c. of water. Saturate 5 c.c. of water with sulphur dioxide and add to 1 litre of water. 50 c.c. of the iodic acid solution and a little starch solution are added to 250 c.c. of water in a cylinder. 50 c.c. of the sulphurous acid are diluted with 250 c.c. of water and the solution is poured quickly into the iodic acid. The liquid remains colourless for an interval and then at once becomes blue. By varying the dilution the time interval may be altered.

Commercial iodine nearly always contains iodine chloride ICl, iodine bromide IBr, and sometimes cyanogen iodide ICN, all of which are

volatile and cannot be separated by sublimation. Resublimation over potassium iodide removes most of the impurity.

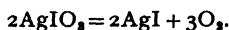
A little iodine is ground in a mortar with potassium iodide and the mixture gently heated in a porcelain dish on a sand-bath. A round-bottom flask filled with cold water is placed over the dish and the purified iodine condenses on its under surface in glittering scales.

Properties.—Iodine forms steel-grey glittering crystals which on heating melt and give off a beautiful violet vapour which dissociates appreciably at high temperatures, $I_2 \rightleftharpoons 2I$, as is shown by the vapour density. Iodine vaporises appreciably at room temperature and has a characteristic smell. It is only slightly soluble in water, forming a yellowish-brown solution. It dissolves readily in hydriodic acid or potassium iodide solutions, forming deep-brown liquids containing HI_3 and KI_3 . It also dissolves in alcohol and ether to form brown solutions, and in carbon disulphide and chloroform to form violet solutions.

The most delicate *test for iodine* is the deep-blue colour which a trace gives with a solution of starch. The colour disappears on heating the solution but reappears on cooling. Iodine also gives a blue colour with solid starch, so that paper (sized with starch) and starched linen are usually turned blue by iodine.

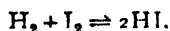
Iodine combines directly with some non-metals, *e.g.* hydrogen (see below), chlorine (forming two solid chlorides ICl and ICl_3) and phosphorus. It combines with many metals on heating forming iodides. It does not, however, react so vigorously as chlorine or bromine.

The **atomic weight of iodine** was determined by Stas by decomposing silver iodate by heat and absorbing the oxygen by red-hot copper :

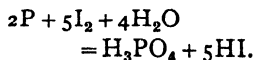


Hence he found the ratio $AgI : O$ and by using the atomic weight of silver he calculated that of iodine. His value found by precipitating silver iodide from a known weight of pure silver in the form of silver nitrate gave a slightly inaccurate result, because the silver iodide carries down a little silver nitrate. The decomposition of pure iodine pentoxide by heat, absorbing the oxygen in red-hot copper, has also been used.

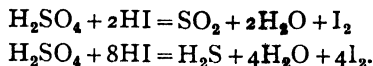
Hydrogen iodide.—Hydrogen and iodine vapour combine to a certain extent in presence of heated platinum (a catalyst) to form gaseous hydrogen iodide (hydriodic acid) but the reaction is incomplete and hydrogen iodide is easily dissociated by heat as it is much less stable than hydrogen chloride or bromide :



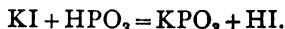
The gas is best prepared by dropping water on a mixture of iodine and red phosphorus (Fig. 103) and collecting by downward displacement :



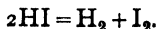
It cannot be prepared in a pure state by heating potassium iodide with sulphuric acid, since the latter is reduced to sulphur dioxide (*cf.* hydrogen bromide) or even hydrogen sulphide, and iodine is liberated :



It may be obtained by heating the iodide with powdered metaphosphoric acid and a little water :



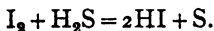
Hydrogen iodide is a colourless gas with a pungent acid smell, which fumes strongly in moist air and is very soluble in water. It is easily decomposed by heat or exposure to sunlight, iodine being set free :



It is more easily liquefied and solidified than hydrogen chloride or bromide.

The composition may be determined by the action of sodium amalgam on the dry gas, as explained in the case of hydrogen bromide (p. 181), the density of iodine vapour (except at high temperature) corresponding with a molecular weight of 2×127 (I_2).

An aqueous solution of hydriodic acid is obtained by passing hydrogen sulphide into a suspension of iodine in water, and filtering from sulphur :



The action ceases at a certain concentration of hydriodic acid but a concentrated solution may be obtained by distilling the solution so obtained. Mainly water distils over at first, then the temperature rises to 127° and a constant boiling solution containing 57 per cent. of hydriodic acid distils over. More concentrated solutions must be prepared from the gas with the apparatus of Fig. 101.

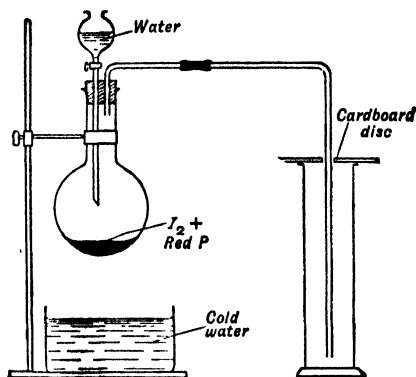
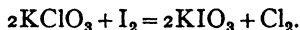


FIG. 103.—Preparation of hydrogen iodide.

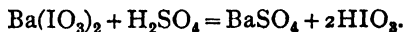
On adding iodine to a hot concentrated solution of potassium hydroxide, sparingly soluble potassium iodate KIO_3 crystallises on cooling :



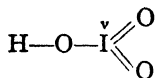
Potassium iodate is also formed by heating a concentrated solution of potassium chlorate with iodine and a little nitric acid :



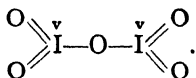
If potassium iodate is added to a solution of barium chloride, barium iodate is precipitated. This is decomposed by dilute sulphuric acid forming iodic acid :



The structural formula of iodic acid is :



and that of iodine pentoxide is



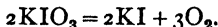
Iodic acid although monobasic forms three series of salts, normal salts and two acid salts :

Normal potassium iodate KIO_3

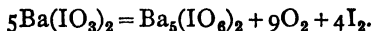
Acid potassium iodate $\text{KIO}_3, \text{HIO}_3$ or $\text{KH}(\text{IO}_3)_2$

Diacid potassium iodate $\text{KIO}_3, 2\text{HIO}_3$ or $\text{KH}_2(\text{IO}_3)_3$.

The normal iodates are sparingly soluble or insoluble in water. Potassium iodate on heating decomposes at a much higher temperature than potassium chlorate and no periodate is formed :

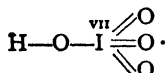


Barium iodate on heating forms a periodate :



Iodates are detected by the blue colour due to liberation of iodine produced when sulphurous acid and starch-paste are added to a solution.

Periodic acid.— HIO_4 , which usually exists in the hydrated form as $\text{H}_4\text{I}_2\text{O}_6$, is a powerful oxidising agent. Its formula is



The halogens.—The group of elements fluorine, chlorine, bromine and iodine show many similarities and are classed together as the halogens (Greek, *hals* = salt). They are all coloured substances with pungent

irritating odours, and their molecules all contain two atoms. Iodine vapour at high temperatures is completely dissociated into atoms: $I_2 \rightleftharpoons 2I$; bromine and chlorine are dissociated to a slight extent at very high temperatures. The elements are univalent and combine with and displace hydrogen atom for atom. They are all strongly electronegative and combine readily with many non-metals and metals, and their compounds show many points of resemblance. Chlorine, bromine and iodine react with alkalis forming chlorides, bromides and iodides together with hypochlorites, hypobromites and hypoiodites when the alkali is in excess and the temperature is not allowed to rise, and chlorides, bromides and iodides with chlorates, bromates, and iodates when the halogen is in excess and the temperature rises. All these compounds have analogous formulae. Fluorine reacts differently with alkalis, an oxide F_2O and an alkali fluoride being formed: $2F_2 + 2NaOH = 2NaF + F_2O + H_2O$. Chlorides, bromides and iodides all give precipitates with silver nitrate solution and the silver salts darken on exposure to light. Silver fluoride is soluble in water.

The stability of the hydrogen compounds as measured by their dissociation on heating is in the order of the heats of formation (p. 395):

	HF	HCl	HBr	HI
k. cal.	38.5	22	12.1	-6.1

(The value for HBr is from liquid bromine, that for HI from *solid* iodine; the formation of HI from iodine *vapour* is exothermic, +9 k. cal.)

Hydrogen iodide is appreciably dissociated at 360° , but hydrogen chloride only slightly at 1000° . The halogens also displace one another from their binary salts in the order of the heats of formation, viz.: $F \rightarrow Cl \rightarrow Br \rightarrow I$. In the oxygen compounds, however, iodine can displace chlorine (p. 190).

Hydrofluoric acid has abnormal properties as compared with the other halogen hydracids probably because it is associated, as is proved by the vapour densities at temperatures below 80° . Its boiling point (19°) is higher than would be expected from the series:



Although the formula H_2F_2 is sometimes assumed for the associated acid there is no direct evidence for it (see p. 176).

CHAPTER XVII

ELECTROLYTES

Electrolysis.—When an electric current is passed through acidulated water decomposition occurs and hydrogen and oxygen gases are produced (p. 38). The process is called **electrolysis**, the acidulated water is called an **electrolyte**, and the platinum plates bringing the current into and out of the solution are called **electrodes**. The electrode connected with the positive pole of the battery is the **positive electrode** or **anode**, that

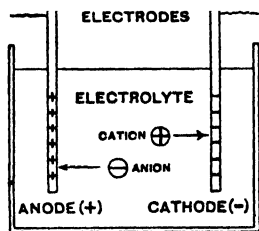
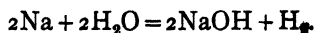


FIG. 104.—Electrolytic cell.

connected with the negative pole is the **negative electrode** or **cathode**. The gases are liberated at the electrodes. The current is carried through the solution by atoms or radicals of the electrolyte, that deposited on the anode being the **negative ion** or **anion**, and that deposited on the cathode the **positive ion** or **cation**. Since unlike charges attract, the charges on the ions are opposite to those on the electrodes at which they appear. These

names are summarised in the diagram in Fig. 104.* The products of electrolysis appear only at the electrodes.

Concentrated hydrochloric acid is decomposed by electrolysis into hydrogen deposited at the cathode and chlorine deposited at the anode (p. 158). Fused sodium chloride is decomposed into metallic sodium deposited on the cathode and chlorine gas deposited on the anode. With a *solution* of sodium chloride, sodium may first deposit on the cathode by a **primary action** (*i.e.* as a direct result of electrolysis) but at once reacts with water by a **secondary action** (*i.e.* one not involving electrolysis), forming a solution of sodium hydroxide and liberating hydrogen gas :



* It should be remembered that the anode is positive but the anion negative, the cathode negative but the cation positive. The names were invented for Faraday by William Whewell and are not really very satisfactory. It is simpler to speak of "positive and negative electrodes" and "positive and negative ions", according to the charges on each.

Chlorine is evolved by a primary action at the anode. Red litmus solution is turned blue around the cathode owing to the alkali but is bleached around the anode by the chlorine.

The primary deposition of sodium occurs on a cathode of mercury connected with the negative wire (Fig. 105), when sodium amalgam is formed and very little hydrogen is evolved. The formation of sodium amalgam is used in the Solvay cell (p. 152).

The distinction between primary and secondary products of electrolysis was made by Faraday in 1833, but more fully and accurately explained by Daniell in 1839. Faraday thought that acids and bases from oxysalts were primary products and metals (*e.g.* lead) were secondary products formed by reduction by hydrogen, whilst Daniell supposed that metals and acid radicals (*e.g.* SO_4) are primary products.

It is now thought that in the electrolysis of sodium chloride solution with platinum or carbon electrodes chlorine is deposited on the anode by a primary process but sodium is not deposited on the cathode. The sodium ions carry the current to the cathode, but hydrogen ions of water deposit on the cathode by a primary process and form hydrogen gas. The hydroxyl ions of the water remain in solution to form a solution of sodium hydroxide with the sodium ions which moved to the cathode. The reaction at the cathode is a decomposition of water :



When a solution of copper sulphate is electrolysed by a current there is a deposit of red metallic copper on the cathode but no gas. At the anode sulphuric acid accumulates and oxygen gas is evolved. The Cu ions of CuSO_4 carry the current to the cathode and are deposited. The SO_4 ions carry the current to the anode. They are not deposited there but water is decomposed. This time oxygen is evolved from hydroxyl ions deposited and the hydrogen ions remain in solution to form a solution of sulphuric acid with the SO_4 ions which moved to the anode :



A solution of sodium sulphate on electrolysis gives sodium hydroxide and hydrogen gas at the cathode, and sulphuric acid and oxygen gas at the anode. The sodium ions carry the current to the cathode and the sulphate ions carry the current to the anode. At the cathode water is

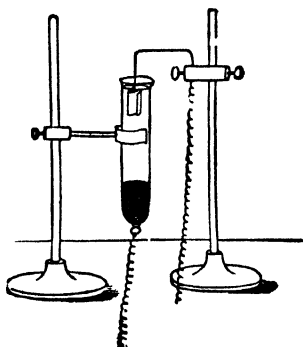


FIG. 105.—Electrolysis with mercury cathode.

decomposed, hydrogen is evolved and the hydroxyl ions form sodium hydroxide solution with the sodium ions. At the anode water is decomposed, oxygen is evolved and the hydrogen ions form sulphuric acid solution with the sulphate ions.

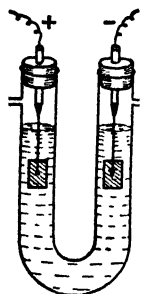
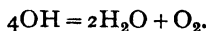


FIG. 106.
Electrolysis of
sodium sulphate
solution.

The production of acid and alkali may be shown by adding purple litmus to the solution of sodium sulphate and electrolysing in a U-tube with platinum electrodes (Fig. 106). The litmus is turned blue by the alkali at the cathode and red by the acid at the anode. The hydrogen and oxygen gases evolved may be collected through side tubes and tested.

In the electrolysis of a solution of sodium or barium hydroxide the sodium or barium ions carry the current to the cathode, where water is decomposed, hydrogen is evolved and hydroxyl ions remain in solution to form sodium or barium hydroxide with the metal ions. The hydroxyl ions of the hydroxide carry the current to the anode and are deposited there, afterwards decomposing by a secondary reaction into oxygen gas and water :



In the electrolysis of dilute sulphuric acid the hydrogen ions of the acid carry the current to the cathode and are deposited. The sulphate ions carry the current to the anode but water is decomposed there, as explained above.

In some cases an ion is *formed* at an electrode, as when a copper anode dissolves during the electrolysis of copper sulphate solution (p. 307).

Faraday's laws of electrolysis.—

The first quantitative investigations of electrolysis were made by Faraday, who in 1832-33 discovered two important laws of electrolysis.*

Faraday connected in series cells containing different electrolytes, with a battery and a water voltmeter for measuring the current (Fig. 107).

His results were comparative, and no absolute units of current were involved in his work.

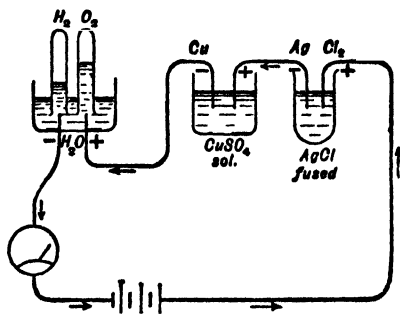


FIG. 107.—Diagram of electrolytic circuit.

* Faraday's papers are reprinted in the *Everyman* series.

Suppose that the first cell contains water acidulated with sulphuric acid, the second a solution of copper sulphate, and the third fused silver chloride, which conducts an electric current.*

After the current has passed for a certain time the volumes of hydrogen and oxygen liberated from the acidulated water, and the weights of copper and silver deposited from the solution of copper sulphate and the fused silver chloride, respectively, can be found. The quantity of electricity which has passed round the circuit is measured by the current strength multiplied by the time. The current strength is measured in amperes; one ampere passing for one second corresponds with unit quantity of electricity, or one coulomb.

If the current passes until 1.008 gm. of hydrogen is liberated from the acidulated water 96,500 coulombs of electricity pass through the cells. If this passes as a small current for a long time (*e.g.* 0.1 ampere for 965,000 sec.) or as a large current for a shorter time (*e.g.* 10 amperes for 9,650 sec.) the result is the same. Hence:

The weight of an ion deposited or formed at an electrode is proportional to the quantity of electricity which passes.

This is Faraday's First Law of Electrolysis.

This may be tested by finding the weight of copper deposited in a copper voltmeter (or coulometer) (Fig. 108) by a steady current in a given time. The copper coulometer consists of two sheet copper anodes *A* and *C* hanging from a bent copper rod *DEFG* supported in two wooden strips, and a thin sheet copper cathode *B*, supported from the copper rod *KL*. The cathode is weighed and the vessel filled with copper sulphate solution. A current of not more than 1/50 amp. per sq. cm. of cathode surface is passed by inserting a suitable resistance and a current-measuring instrument in series with the coulometer and a battery. After a suitable time the cathode is taken out, washed, dried and weighed to find the weight of copper deposited. The experiment is repeated with the same current but twice the time, when twice as much copper will be found to have been deposited as in the first experiment. Keeping the time the same as in the first experiment, the current strength is now reduced to half by a suitable resistance in series, when the weight of copper deposited will be half the previous weight.

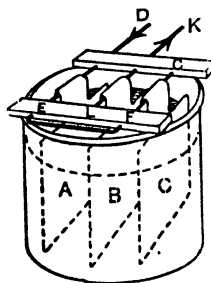


FIG. 108.—Copper coulometer.

* Faraday used fused stannous chloride, which was decomposed into tin and chlorine, but the chlorine at once combined with stannous chloride to form stannic chloride, which volatilised. He found that 3.2 grains of tin were set free by the same current which liberated 3.85 cubic inches of electrolytic gas in a voltmeter (he does not specify temperature and pressure), and hence he calculated the equivalent of tin as 57.9 instead of 58 found by the chemical method (modern value = 59 when $H=1$). Faraday also used fused lead chloride with a carbon anode. Fused silver chloride gave him trouble because the silver crystals grew across to the anode and short-circuited the current.

The weights of the other ions deposited in the cells whilst 1.008 gm. of hydrogen is liberated from the water are found to be *equivalent weights* : 8 gm. of oxygen, 35.5 gm. of chlorine, 31.5 gm. of copper and 107.9 of silver. Thus :

The weights of the different ions deposited or formed by the same quantity of electricity are in the ratios of their chemical equivalents.

This is Faraday's Second Law of Electrolysis, more concisely expressed in the form : 96,500 coulombs deposit or form one gram-equivalent of any ion in electrolysis. This quantity of electricity is called a *faraday* and denoted by *F*.*

Faraday's second law may be tested by passing the same current through three cells in series containing : (i) acidulated water in a water voltmeter (p. 39) ; (ii) copper sulphate solution with copper electrodes in a copper coulometer ; and (iii) a solution of silver nitrate in a silver coulometer (p. 323). The volumes of hydrogen and oxygen, and the weights of copper and silver deposited, are found. The weights should be in the ratio of the equivalents, viz. 1.008, 8, 31.5 and 107.9.

Faraday's second law provides a method of finding the equivalent of an element ; for example, the equivalents of copper and silver could be determined in the experiment described.

The theory of electrolysis.—Since the ions appear only at the electrodes it is simplest to assume that they are themselves charged, the sign of the charge on an ion being *opposite* to that of the electrode towards which it moves by attraction. Thus :

Anions are negatively charged atoms or radicals and cations are positively charged atoms or radicals.

The electricity is ferried across from one electrode to the other by the charged ions, and this electrolytic current completes that passing through the circuit outside the cell. *The strength of the current is uniform throughout the whole circuit*, whether the latter is all metallic or is composed of metal wires and electrolytes. Since the current in the electrolyte is composed solely of charged ions, the weight of an ion moving to an electrode is proportional to the current strength and the time, or to the quantity of electricity. This is Faraday's First Law.

Faraday's Second Law is explained by assuming that :

The electric charge on an ion is the same for all ions of the same valency and is proportional to the valency.

Thus, a univalent cation such as sodium carries unit positive charge ; a bivalent cation such as copper carries 2 unit positive charges ; a univalent anion such as chlorine carries a unit negative charge equal but *opposite* to the unit positive charge on the sodium ion ; a bivalent negative ion such

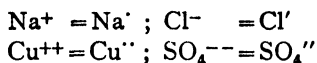
* Not to be confused with the *farad*, the unit of capacity.

as SO_4 carries 2 unit negative charges. In general, if e is the unit charge then the charge carried by an ion of valency n is $\pm ne$, positive or negative. A positive charge carried in one direction is equivalent to an equal negative charge carried in the opposite direction.

When the charge e passes round the circuit it carries amounts of ions in the electrolyte equal to their atomic or molecular weights divided by n , and deposits them on the electrodes. Hence the same quantity of electricity deposits weights of ions in the ratios of their equivalents. This is Faraday's Second Law.*

The electron.—The constant electric charge on univalent ions and the simple multiple relation between the charges on multivalent ions suggest that electricity like matter is divided into atoms. This was suggested by Maxwell in 1873, with some reserve, and in 1874 G. J. Stoney calculated this unit charge, which he called an **electron**. Helmholtz † in 1881 said: "The most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also is divided into definite elementary portions, which behave like atoms of electricity." The *free* atom of electricity is the *negative* electron and an atom which has gained one electron has unit negative charge, whilst an atom which has lost one electron has unit positive charge. The hydrogen atom which has lost one electron is the positively charged **proton**. The mass of the electron is only about $1/1840$ that of the hydrogen atom or proton.

For convenience, the + or - charge of an ion is often represented by a dot or a dash :



Theory of electrolytic dissociation.—All experiments on electrolysis can be explained by the simple assumption that the ions move independently in electrolytes. They behave as if they were free and each ion moves to an electrode as if the others were absent.

Since any applied E.M.F., however small, will produce electrolysis if polarisation (which opposes the electrolysing E.M.F.) is eliminated, it seems that no work is spent in breaking up the electrolyte molecules. Clausius in 1857 assumed that these molecules are already broken up in the solution and the only action of the current is to guide the free charged ions to the electrodes. Since the dissociation of common salt into sodium and chlorine in solution seemed inconsistent with ordinary chemistry, Clausius assumed that only a very small fraction of the molecules was

* It must not be thought that Faraday gave this explanation; his ideas are not easy to understand and the present theory is due to Helmholtz.

† Faraday Lecture, 1881, in *Chemical Society Faraday Lectures*, 1928, p. 132.

ionised, this process going further as the ions are removed. A similar view was held for chemical reactions generally by Williamson in 1850.

In 1887 Arrhenius * assumed that a salt in solution is generally practically *completely* dissociated into charged ions. This is called **electrolytic dissociation**. In a solution of sodium chloride the salt does not exist as sodium chloride molecules, NaCl , but as charged sodium ions Na^+ and chlorine ions Cl^- . Copper sulphate exists as Cu^{++} and SO_4^{--} ions.

It should be noted that the sum of the charges on the cations in a solution must always equal the sum of the charges on the anions, since the whole solution is uncharged; *e.g.* Cu^{++} and SO_4^{--} and 2Na^+ and SO_4^{--} .

In electrolysis, a Cl^- ion reaching the anode gives up an electron and forms a chlorine atom Cl . Chlorine atoms combine to form chlorine gas Cl_2 . The electron can pass round the metal circuit and electrons at the cathode can neutralise positive ions which deposit there, *e.g.* H^+ ions form H atoms and these form hydrogen gas H_2 . (See p. 193).

The migration of ions.—The bodily transfer of ions in solution in an electric field can be shown by the apparatus of Fig. 109.

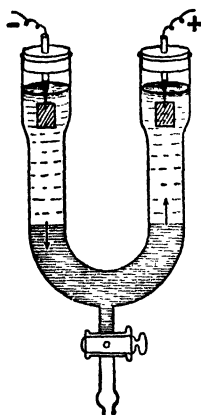


FIG. 109.—Demonstration of ionic migration.

The U-tube is half-filled with a *weak* solution of potassium nitrate. By connecting a funnel with the tap below, a solution of potassium permanganate is slowly admitted. The surface of separation between the colourless liquid above and the purple solution below should be sharp. A current is now passed between the platinum electrodes. The purple MnO_4^- ions move to the anode and the levels alter as shown. If the levels are marked by thin strips of gummed label, the change is apparent after 10-15 minutes.

This experiment shows that the speed of the ions in bulk is very slow. They meet with great resistance from the water molecules, and Kohlrausch calculated the total force required to propel 1 g. mol. of potassium ions through a solution with a speed of 1 cm. per sec. as one and a half million tons.

Equivalent conductivity.—In a cell containing two platinum electrodes 1 sq. cm. in area placed parallel to each other at a distance of 1 cm. apart, the current in amperes which passes through a solution of an electrolyte

* His paper is translated in *Alembic Club Reprint No. 19*.

between the plates when the latter are at a difference of potential of 1 volt is called the **conductivity** (sometimes **specific conductivity**) of the solution, denoted by κ .

The conductivity depends on the concentration. In a solution containing 1 gm. equivalent of electrolyte per litre (*e.g.* HCl or KCl or $\frac{1}{2}\text{H}_2\text{SO}_4$ or $\frac{1}{2}\text{CuSO}_4$) we have a certain number of ions between the electrodes in the cell and the current carried by these ions is equal to the conductivity. If we dissolve twice as much electrolyte in a litre, the actual conductivity will be greater although there may really be a smaller fraction of molecules broken up into ions than in the more dilute solution. Again, if we dilute the solution containing 1 gm. equiv. per litre to one containing 0.01 gm. equiv. per litre, the actual conductivity will be less as there are fewer ions between the electrodes although a larger fraction of molecules may be ionised. To make a fair comparison between the ionisations we must divide the conductivity κ by the number c of gm. equiv. of salt *per c.c.*, and the quotient κ/c is called the **equivalent conductivity**, denoted by Λ .

The equivalent conductivity :

$$\Lambda = \frac{\kappa}{c}$$

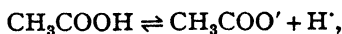
increases with dilution and reaches a maximum Λ_∞ or Λ_0 , as the dilution becomes infinite or the concentration zero. This is called the **equivalent conductivity at infinite dilution**.

This result can be explained in two ways. (1) It may be assumed that the electrolyte is completely dissociated into ions at all concentrations, but the speeds of the ions increase as the solution becomes more dilute, until in very dilute solution the ionic speeds (for a given potential gradient between the electrodes) become constant. Or (2) it may be assumed that the speeds of the ions are practically constant at the various concentrations but the dissolved electrolyte is incompletely ionised, the ionisation increasing with dilution until at very high dilutions the electrolyte is completely ionised.

On the second assumption the ratio of the equivalent conductivity Λ_v at any dilution v to that at infinite dilution Λ_∞ when all the electrolyte is ionised gives the **degree of ionisation** α at the given dilution : $\Lambda_v/\Lambda_\infty = \alpha$.

The dilution is the reciprocal of concentration, *i.e.* v is the number of c.c. containing 1 gm. equivalent of total electrolyte. In practice, the concentration is usually measured in gm. equiv. per litre and the dilution in litres per gm. equiv.

Electrolytes such as acetic acid which are only slightly ionised in solution are called **weak electrolytes** :



and their degree of ionisation is given by the ratio Λ_v/Λ_∞ .

Electrolytes such as sodium chloride and hydrochloric acid which are largely ionised in solution (over 90 per cent.) are called **strong electrolytes** and are now regarded as practically completely ionised. On account of the electrical interaction of the oppositely charged ions the change of equivalent conductivity on dilution is due almost entirely to changes in ionic speed, and the ratio Λ_0/Λ_∞ no longer measures the degree of ionisation, which is practically 1.

Determination of conductivity.—The conductivity of an electrolyte is measured with an alternating current from a small induction coil, the

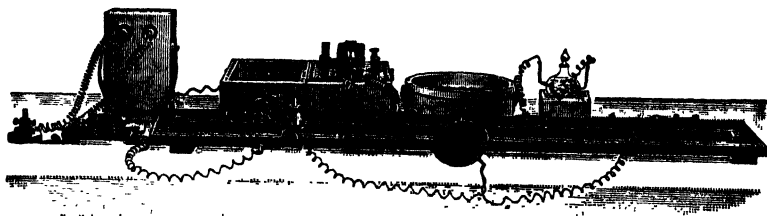


FIG. 110.—Apparatus for measurement of conductivity.

solution being contained in a cell with platinised platinum plates as electrodes. This arrangement eliminates polarisation of the electrodes.

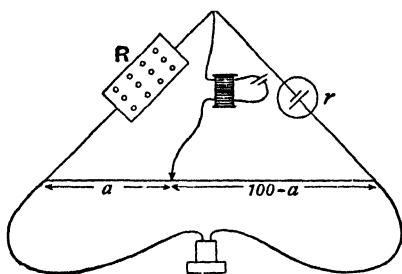


FIG. 111.—Diagram of conductivity apparatus.

The cell is shown on the right in Fig. 110. The platinum wires attached to the electrodes are sealed into mercury contacts, from which wires are taken to a Wheatstone bridge arrangement shown in Fig. 111: r is the cell and R a resistance box, a metre wire bridge with a sliding contact being connected with the coil and telephone as shown. The telephone is used as a detector of alternating current and the bridge is balanced when the sound in

the telephone is a minimum. The cell should be in a water bath of constant temperature, preferably in a thermostat, since the conductivity increases rather considerably with temperature. The temperature coefficient of the equivalent conductivity, $\frac{1}{\Lambda} \cdot \frac{d\Lambda}{dt}$, is about 2 per cent. per degree, so that the temperature should be constant to 0.01° . Measurements are usually made at 18° or 25° .

The resistance of the conductivity cell is given by the Wheatstone bridge formula $\frac{R}{r} = \frac{a}{100-a}$; $\therefore r = R \times \frac{100-a}{a}$ ohms. Ohm's law has been proved

experimentally to apply to electrolytes. The conductance is $1/r$, i.e. the current in amperes for 1 volt potential difference between the electrodes.

The electrodes of the conductivity cell will not usually be exactly 1 sq. cm. in area, parallel, and 1 cm. apart, so that the conductance $1/r$ is not usually equal to the conductivity κ . Since the relation between the two depends only on the construction of the cell, it is possible to determine this once for all by using as electrolyte a solution of known conductivity, viz. a normal solution of potassium chloride for which at 18° $\kappa_{18^\circ} = 0.09822$. If the resistance of the cell containing this solution is r , $\kappa_{18^\circ} = C/r = 0.09822$, where C is the cell constant. If any other solution is used, and if the resistance is r' ohms, the conductivity is $\kappa'_{18^\circ} = C/r'$.

Kohlrausch's law.—The independent movement of the ions of a salt which is assumed in the theory of electrolytic dissociation gives a simple explanation of a result discovered experimentally by Kohlrausch in 1875 and known as Kohlrausch's law: *the equivalent conductivity of a salt at infinite dilution is the sum of two parts, one depending only on the cation and the other only on the anion:*

$$\Lambda_\infty = l_+ + l_-.$$

Λ_∞		Λ_∞
KCl 130.0		NaCl 108.9
KNO ₃ 126.3		NaNO ₃ 105.2
$\Lambda_\infty \text{KCl} - \Lambda_\infty \text{KNO}_3 = 3.7$		$\Lambda_\infty \text{NaCl} - \Lambda_\infty \text{NaNO}_3 = 3.7$
$\Lambda_\infty \text{KCl} - \Lambda_\infty \text{NaCl} = 21.1$		$\Lambda_\infty \text{KNO}_3 - \Lambda_\infty \text{NaNO}_3 = 21.1$

The value 3.7 is the difference in l_a values for Cl and NO₃, and the value 21.1 is the difference in l_c values for K and Na: l_a and l_c are called the mobilities of the anion and cation, respectively, expressed in conductivity units.

The migration of ions.—The unequal speeds of different ions causes changes of concentration of *salt* (not ions separately) around the electrodes. These changes were related to the ionic speeds by Hittorf in 1853.

In Fig. 112 the black and white circles represent cations and anions, in the upper row *a* before electrolysis and in the lower row *b* after. The

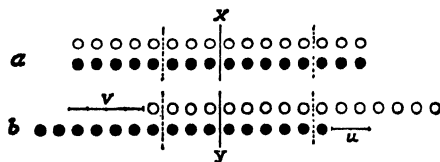


FIG. 112.—Migration of ions.

black circles move to the left with a speed u and the white circles to the right with a speed v which in the case considered is twice as great as u . The vertical line xy divides the arrangement into two equal parts.

Before electrolysis there are eight black and white ions on each side. After electrolysis six equivalents of salt have been decomposed and the

unpaired ions deposited; there are four undecomposed equivalents of salt on the left and six on the right, so that four equivalents of salt have been lost on the left and two on the right. *The losses in neutral salt molecules around the electrodes are in the ratio of the speeds of the ions migrating away from the electrodes.*

The fractions of the total current carried by the cation and anion, respectively, are one third and two thirds, or generally

$$u/(u+v) \quad \text{and} \quad v/(u+v)$$

or since

$$\Lambda_{\infty} = l_c + l_a$$

$$l_c/\Lambda_{\infty} = u/(u+v); \quad l_a/\Lambda_{\infty} = v/(u+v).$$

The fraction of the total current carried by an ion is called the **transport number** n . It is not, like the mobility, a constant depending only on that ion, but varies from salt to salt according to the mobility of the other ion. If we refer n to the anion, then:

$$l_a/l_c = n/(1-n),$$

and from n and $\Lambda_{\infty} = l_c + l_a$, we can calculate l_c and l_a separately.

MOBILITIES IN AQUEOUS SOLUTION AT 18°.

Cations l_c		Anions l_a	
Na'	43.3	Cl'	65.3
K'	64.5	Br'	67.3
NH ₄ '	64.5	I'	66.1
H'	315.6	NO ₃ '	61.6
Ag'	54.0	OH'	174
$\frac{1}{2}$ Zn''	46.7	CH ₃ COO'	35
$\frac{1}{2}$ Cu''	45.5	$\frac{1}{2}$ SO ₄ ''	67.9
$\frac{1}{2}$ Ba''	55.0	$\frac{1}{2}$ CO ₃ ''	60

The large mobilities of the hydrogen and hydroxide ions should be noted.

The value of Λ_{∞} for a weak acid such as acetic is found by adding 315.6, the mobility of the hydrogen ion, to the mobility of the anion, *e.g.* 35 for the acetate ion CH₃COO', $\therefore \Lambda_{\infty}$ for acetic acid = 315.6 + 35 = 350.6.

The solubility of a sparingly soluble salt may be determined from the conductivity of the saturated solution.

The specific conductivity κ of saturated silver chloride solution at 18°, after suitable correction by subtraction of the conductivity of the water used, is 1.24×10^{-6} ohm⁻¹. cm.⁻¹, and since the solution is very dilute it may be considered completely ionised. Now $\Lambda = \kappa/c$ and in this case Λ may be taken as $\Lambda_{\infty} = 54.0 + 65.3 = 119.3$;

$$\therefore c = 1.24 \times 10^{-6} / 119.3 \times 10^3 = 1.04 \times 10^{-8} \text{ equiv. per c.c.}$$

Absolute speeds of ions.—Let a completely ionised solution of 1 gm. equiv. of salt be electrolysed with a potential gradient of 1 volt per cm.

The ions move with speeds of u and v cm. per sec. and the charges transported per sec. are $+uF$ and $-vF$, where $F=1$ faraday = 96,500 coulombs. Negative charge moving in one direction is equivalent to positive charge moving in the opposite direction, hence the total charge transported per sec. is $uF+vF$, which is the same as the current, viz. $A_{\infty}=I_e+I_a$. Hence:

$$I_e+I_a=F(u+v) \quad \text{or} \quad I_e=Fu \quad \text{and} \quad I_a=Fv.$$

Hence the mobilities u and v expressed in cm. per sec. for a potential gradient of 1 volt per cm. can be calculated from the values of I_e and I_a in the above table. In this way the following values were found: they are confirmed by direct measurements as described on p. 198:

H'	0.00326	OH'	0.00181
K'	0.00067	NO ₃ '	0.00064
Ag'	0.00057	I'	0.00069
Na'	0.00045	Cl'	0.00068
NH ₄ '	0.00066	SO ₄ ''	0.00071

Strengths of acids.—Acids in solution owe their acidic properties to the hydrogen ion, and their relative strengths may be compared by measuring the relative ionisations in solutions containing equivalent weights of the acids in identical volumes. The ionisation is most conveniently determined by the conductivity. Since the hydrogen ion is much more mobile than any of the anions of acids (as is seen from the table above) it carries most of the current and the relative conductivities are therefore *approximately* proportional to the ionisations.

Distilled water and $N/50$ solutions of acetic, sulphuric, and hydrochloric acids are poured into tubes fitted with platinum or copper electrodes (Fig. 113). The electrodes are the same distance apart and in series with each tube is a carbon-filament lamp. The tubes are connected in parallel with the mains. The lamps in circuit with the water and acetic acid remain dark because the conductivities are so small that hardly any current passes. The lamps connected with the hydrochloric and sulphuric acids light up and the former is brighter than the latter. The order of conductivities of the three acids: $\text{HCl} > \text{H}_2\text{SO}_4 > \text{CH}_3\text{CO}_2\text{H}$, is the same as the order of strengths.

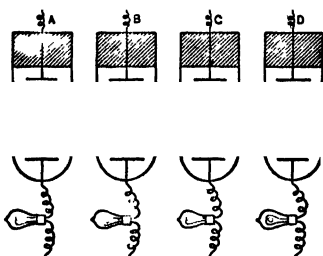
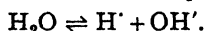


FIG. 113.—Comparison of conductivities of acids.

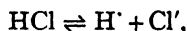
The purest water which can be obtained is almost but not quite a non-conductor of electricity. After allowing for the effects of traces of conducting impurities, a slight conductivity remains which is due to the

ions of water itself. The ionisation of water into hydrogen ions and hydroxide ions is very small and a state of equilibrium is set up :



Water is ionised only to the extent of 1 mol in 10^{10} c.c. at room temperature.

If 1 mol of hydrochloric acid is dissolved in water so that the total volume of solution is 1 litre, the conductivity increases nearly ten million-fold. This is due to the ionisation of the hydrochloric acid :

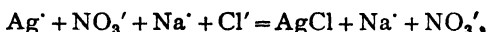


the ions of which are present in very great numbers as compared with the ions of water.

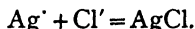
Reactions between ions.—Since most salts are largely ionised in solution, the reactions between them usually occur between their ions. On adding a solution of sodium chloride to one of silver nitrate, the silver ion and chloride ion form insoluble silver chloride which is precipitated, whilst the sodium and nitrate ions take no part in the reaction and remain in solution. Instead of the equation :



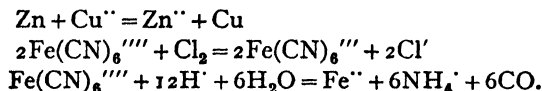
a more correct representation is :



or since the sodium and nitrate ions are not concerned :



A necessary condition for the correctness of an ionic equation is that the sum of the positive and negative ionic charges shall be the same on both sides :



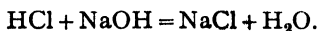
Oxidation and reduction.—Metallic sodium and iron may be regarded as discharged ions possessing zero charge, Na^0 and Fe^0 . In converting an atom of iron into a ferrous ion two electrons are removed producing Fe^{2+} . When this is converted into the ferric ion another electron is removed producing Fe^{3+} . **Oxidation** therefore corresponds with increasing positive charge or increasing the valency of a cation. **Reduction** is equivalent to diminution of positive charge or increase of negative charge, *i.e.* increasing the valency of an anion. Ferricyanides are reduced to ferrocyanides by increasing the negative charge on the ion by one unit : $\text{Fe}(\text{CN})_6^{3-} + e = \text{Fe}(\text{CN})_6^{4-}$, where e is the electron. Iron in chlorine water forms ferric chloride, *i.e.* ferric ions and chloride ions, and the

metallic iron has been oxidised : $\text{Fe} - 3e = \text{Fe}'''$, whilst the free chlorine has simultaneously been reduced : $3\text{Cl} + 3e = 3\text{Cl}'$.

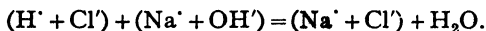
The **electrovalency** of an ion is equal to its charge, +3 for the ferric ion and -4 for the ferrocyanide ion. It represents the number of electrons lost or gained by the neutral atom or radical in forming the ion. This is an extension of the idea of valency, since sodium chloride in solution is not $\text{Na} - \text{Cl}$ but Na^+ and Cl^- as two separate ions.

Neutralisation.—Acids are substances producing the hydrogen ion in solution : $\text{HCl} \rightleftharpoons \text{H}' + \text{Cl}'$. Bases are substances producing the hydroxide ion in aqueous solution : $\text{NaOH} \rightleftharpoons \text{Na}' + \text{OH}'$.

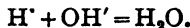
When an acid and base in solution are mixed a salt is formed and the solution becomes neutral. This is usually represented as :



Since the acid, base and salt are ionised, the reaction occurs between the ions :



The Na' and Cl' the ions of the salt take no part in the change and are free before and after the reaction. Hence *neutralisation is the union of the hydrogen ion of the acid with the hydroxide ion of the base to form practically undissociated water* :



The hydrogen and hydroxide ions possess the greatest mobility, and on neutralisation, when these ions are withdrawn, the conductivity diminishes. This is shown by the following experiment.

Fit a rectangular glass trough with two electrodes of sheet copper (Fig. 114). Connect these through an ammeter with two accumulators in series. Pour into the cell *N*-NaOH solution containing urea to increase its density and coloured with phenolphthalein. Float a slice of cork on this solution, and by means of a burette introduce an equal volume of *N*-hydrochloric acid as a definite stratum above the alkali. Switch on the current and observe the deflection of the ammeter. This is a measure of the current carried by all the ions, Na' , H' , OH' , Cl' . Now stir the two liquids with a glass rod and notice the reduced reading of the ammeter. The ions Na' and Cl' alone now carry the current.

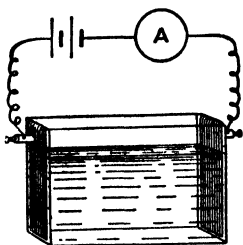
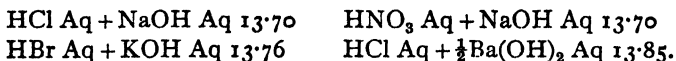


FIG. 114.—Diminution of conductivity on neutralisation.

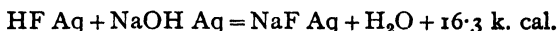
The heat evolved in the neutralisation of one equivalent of a strong base by one equivalent of a strong acid should be the same for different acids and bases, since the reaction in all cases is the union of hydrogen

ion from the acid with hydroxide ion from the base to form undissociated water.

This is verified by experiment; the heat of neutralisation per equivalent of *any* strong acid and base is equal to about 13.7 k. cal.



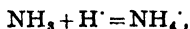
If the acid or the base is weak the un-ionised acid or base will dissociate as neutralisation proceeds, and this dissociation absorbs or evolves heat. An example of this is the neutralisation of hydrofluoric acid:



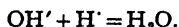
Thus, heat is evolved in the ionisation of HF.

***Theory of acids and bases.**—In aqueous solutions of acids the hydrogen ion is probably attached to a molecule of water, forming the **hydroxonium ion**: $\text{H}^+ + \text{H}_2\text{O} = \text{H}_3\text{O}^+$. Regarded as the result of the removal of an electron from a hydrogen atom, the H^+ ion is the free proton (p. 261) and this could scarcely be expected to exist in the free state in solution to any appreciable extent. The hydrogen ion is probably also *solvated* in other media besides water.

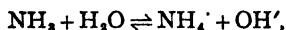
In the theory of acids and bases developed by Arrhenius, the hydroxide ion of bases occupied a position as unique as the hydrogen ion of acids. Another theory first developed by Lapworth (1908) defines a base as *a substance which unites with hydrogen ion*, or in the more hypothetical terminology of modern theory *a base is an acceptor of protons whilst an acid is a donor of protons*. Whereas all acids have a common property this is not necessary in the case of bases. A neutral ammonia molecule may accept a proton to form the ammonium ion and thus functions as a base:



and this is just as much a neutralisation reaction as the acceptance of a proton by the hydroxide ion:

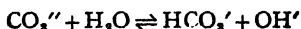


The NH_3 molecule may abstract protons from water:



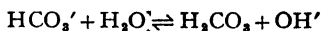
and in this case the greater strength of ammonia as compared with water as a base is shown by the appearance of OH^- ions, *i.e.* by an alkaline reaction.

The anion of any weak acid is able to function as a strong base. In aqueous solutions of sodium carbonate the CO_3^{--} ions withdraw hydrogen ions from the water, forming the bicarbonate ion:



* This section may be omitted.

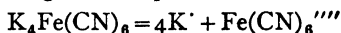
and the very weak carbonic acid :



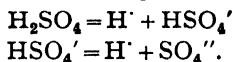
and leaving the hydroxide ions of the water, which make the solution alkaline and "basic". Reactions of this type are called **hydrolysis** (p. 238).

Modern theory of strong electrolytes.—Modern theory assumes that strong electrolytes are practically completely ionised at dilutions greater than $0.1N$ and that the change of conductivity with concentration is due, not to changes in the number of ions with constant speeds as in Arrhenius's theory, but to changes of speed with constant number. In the theory of Debye and Hückel (1923) the electrical forces between the charged ions are assumed to reduce the conductivity Λ_∞ , which would be shown if the ions exerted no influence on one another, to $\Lambda = \Lambda_\infty - a\sqrt{c}$, where c = concentration and a is a constant. Thus Λ when plotted against the square root of the concentration gives very nearly a straight line at small concentrations. This was discovered empirically by Kohlrausch many years ago. The theory shows that the slope of the Λ and \sqrt{c} curves should be greater with ions of higher valency (*e.g.* Cu'' , SO_4'') and this also had been found by Kohlrausch.

Ionisation in stages.—Molecules capable of giving more than two ions often dissociate in stages, but not always. Potassium ferrocyanide ionises directly according to the equation :

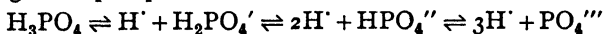


whilst sulphuric acid ionises in two stages :



The ionisation in the second stage is small except in very dilute solutions. At moderate dilutions sulphuric acid behaves as a monobasic acid as the conductivity shows. But if the acid is neutralised with a base, the hydrogen ion combines with the hydroxide ion of the base to form water : $\text{H}_2\text{SO}_4 + 2\text{OH}' = \text{SO}_4'' + 2\text{H}_2\text{O}$. As the hydrogen ion corresponding with the first stage of the ionisation is removed the HSO_4' ion dissociates. This goes on until all the HSO_4' has been ionised and finally only SO_4'' ions remain, which correspond with the formation of the normal salt. Thus the acid behaves as dibasic.

The later stages of ionisation of polybasic acids are almost always small ; *e.g.* with phosphoric acid :



the last stage is so slight that the PO_4''' ion in a solution of Na_3PO_4 acts as a strong base : $\text{PO}_4''' + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4'' + \text{OH}'$.

Evidence for the theory of electrolytic dissociation.—The main lines of evidence for Arrhenius's theory may be summarised as follows* :

(1) It explains all the facts of electrolysis and is not contradicted by experiments in other fields.

* See Arrhenius, "Faraday Lecture", *J. Chem. Soc.*, 1914.

(2) It explains why the equivalent conductivity of an electrolyte increases with dilution to a fixed maximum limit (Λ_{∞}).

(3) It accounts for the fact that the properties of an electrolyte solution are additively composed of the properties of the ions.

(4) It explains reactions in qualitative analysis, *e.g.* why all chlorides (Cl^-) give the same reaction with silver nitrate whilst chlorates (ClO_3^-) do not give this reaction.

(5) It explains the effect of an excess of reagent on the solubility of a precipitate ("solubility product effect", see Chapter XIX), including the "abnormal" cases when complex ions are formed.

(6) It gives an explanation of "abnormal" osmotic pressures, freezing point depressions and boiling point elevations shown by electrolytes, and the values of α (extent of ionisation) calculated from the conductivity agree with those found by the osmotic methods.

(7) It explains the constant heat of neutralisation of strong acids and bases.

(8) The "anomalies" of strong electrolytes, *e.g.* their deviation from Ostwald's Dilution Law (see Chapter XIX) are explained by an extension of the theory in which ionisation is still assumed.

(9) It explains the action of voltaic cells.

(10) It is in good agreement with recent theories of the structure of the atom.

All the so-called "objections" to the theory are based on misunderstanding or faulty experiments or interpretations and need not be stated.

Decomposition potentials.—Although the deposition of a gm. equiv. of any ion requires the passage of the same *quantity* of electricity (96,500 cmb.) the *energy* is different for different ions, and since this is the product of coulombs and volts it follows that the decomposition potentials are also different. A Daniell's cell (1.1 volts) will not decompose water whilst an accumulator (2 volts) will do so.

When decomposition proceeds, the electromotive force set up by the products of decomposition acting as a cell must be overcome before further deposition can occur.

DECOMPOSITION VOLTAGES IN N-SOLUTIONS

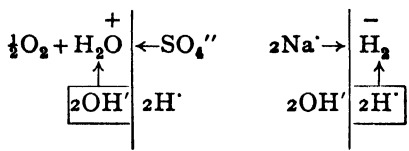
HNO_3	1.69	NaOH	1.69	ZnSO_4	2.35
H_2SO_4	1.67	KOH	1.67	NaNO_3	2.15
HCl	1.31	AgNO_3	0.70	NaCl	1.98
HBr	0.94	ZnBr_2	1.83	CaCl_2	1.89
HI	0.52				

In practice a larger potential may be required to deposit an ion than the theoretical electrode potential, especially when hydrogen gas is being liberated; the excess is called the **overvoltage** of the ion. For hydrogen this is very small on platinised platinum but large on amalgamated lead.

The formation of sodium amalgam in the Solvay cell (p. 153) is possible in spite of the fact that the potential required to deposit sodium is much higher than that normally required to deposit hydrogen. Hydrogen, however, has a large overvoltage on mercury so that sodium is deposited instead. In order to dissolve the sodium from the amalgam to form sodium hydroxide and hydrogen, the amalgam is brought in conducting contact with metallic iron, on which hydrogen has a small overvoltage. Gaseous hydrogen from the water is formed on the iron and the sodium passes into solution as ions, the hydroxide ions of the water remaining in the solution.

The table shows that for solutions of salts *when only hydrogen and oxygen are deposited*, the decomposition voltages are often practically the same. Le Blanc assumed that in *all* these cases *the current is carried through the solution by the ions of the salt but the ions of water H^+ and OH^- , being more easily deposited and at a lower voltage than the metal or acid ions, are deposited at the electrodes* forming hydrogen and oxygen gases. The other ion of water remains in solution at the corresponding electrode, forming acid or alkali with the salt anion or cation which has arrived there after carrying the current through the solution to the electrode.

In the electrolysis of a sodium sulphate solution, the sodium and sulphate ions are present in large amounts and carry the current through the solution. At the electrodes these ions are not discharged, since the hydrogen and hydroxide ions of water are more easily discharged. The result is :



That is, $2NaOH + H_2$ are formed at the cathode and $H_2SO_4 + \frac{1}{2}O_2 + H_2O$ at the anode.

Only very small amounts of hydrogen and hydroxide ions are present in the water but as fast as they are discharged fresh supplies are formed by the ionisation of the water. The decomposition potentials of salt solutions giving only hydrogen and oxygen are rather larger than those of acids and bases. This is because alkali forms at the cathode and acid at the anode, and hydrogen and oxygen are liberated from alkaline and acid solutions, respectively, which is the reverse of the normal case.

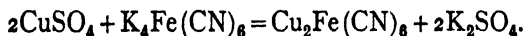
In the decomposition of HCl , HBr and HI the potentials are smaller, since halogens and not oxygen are liberated at the anode, and with $AgNO_3$ silver and not hydrogen is liberated at the cathode.

CHAPTER XVIII

MOLECULAR WEIGHTS IN SOLUTION

Osmotic pressure.—When a concentrated solution of copper sulphate in the lower part of a cylinder is covered with a layer of water, the copper sulphate gradually *diffuses* upwards until the solution becomes homogeneous and of uniform colour. The dissolved molecules behave to some extent like a gas ; they are in motion and possess kinetic energy. If we could interpose a partition in the solution which would stop the dissolved molecules but would be freely permeable to pure water, we should expect the copper sulphate ions to exert a pressure on the partition. A partition which freely lets through the pure solvent but stops the dissolved substances is called a **semipermeable partition** or—since it is usually prepared in the form of a thin film—a **semipermeable membrane**.

Various substances form semipermeable membranes. If a drop of copper sulphate solution is introduced from a pipette into a solution of potassium ferrocyanide a skin forms over it, composed of copper ferrocyanide produced as a reddish-brown gelatinous precipitate when the two solutions are mixed :



The pellicle is semipermeable, because no copper salt diffuses through the drop, the ferrocyanide solution remaining clear. The drop expands or shrinks on standing owing to passage of *water* through the pellicle. By holding the drop suspended with a bright light behind the beaker, the streaks due to changes of concentration may be seen.

An interesting experiment is the " Chemical Garden " first described by Glauber in 1648. A clear solution of sodium silicate of sp. gr. 1.1 made by diluting " water glass " is poured into a tall cylinder and small pieces of ferric, nickel, cobalt, copper and manganous chlorides are dropped in. After a few hours long coloured growths of gelatinous silica coloured by metal hydroxides grow from the crystals. A semipermeable film of silica is formed round each crystal and water enters through this and bursts the film, the salt solution driven out being at once covered by a further film, and so on.

Measurement of osmotic pressure.—The copper ferrocyanide membrane is too weak to stand pressure, so Pfeffer in 1877 formed it in the walls of an earthenware porous pot (Fig. 115).

The pot is immersed in copper sulphate solution and placed under the receiver of an air-pump. The air in the pores is removed and on admitting air to the receiver, the solution is forced into the pores. The pot is removed from the solution, quickly washed out, and filled up with 3 per cent. potassium ferrocyanide solution. The pot is then allowed to stand for several hours in copper sulphate solution. The two salts diffuse through the porous wall, meeting somewhere inside and producing a coherent film of copper ferrocyanide in the wall of the pot. (The preparation of a good semipermeable pot is difficult; most of the results are failures and many precautions must be taken which cannot be described here. Better results are said to be obtained by driving the ions Cu^{++} and FeCy_6^{++++} by electrolysis into the pot.)

The pot is filled up with a solution (say of sugar in water), fitted with a manometer and plunged into water, when there is a gradual rise of pressure until a steady value is finally reached. This is the **osmotic pressure** of the solution. In order to squeeze pure solvent through a semipermeable membrane a definite pressure must be applied to the solution enclosed in it. At lower pressures no solvent percolates through.

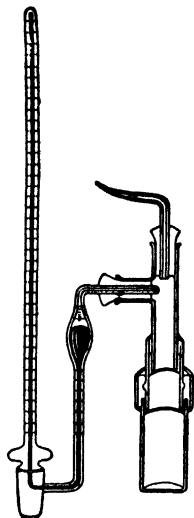


FIG. 115.—Pfeffer's apparatus.

Berkeley and Hartley measured the osmotic pressures of *concentrated* solutions with an apparatus (Fig. 116) in which the tube *C* carrying the semipermeable membrane is filled with water and surrounded by the solution to which a pressure *P* is applied to balance the osmotic pressure. The

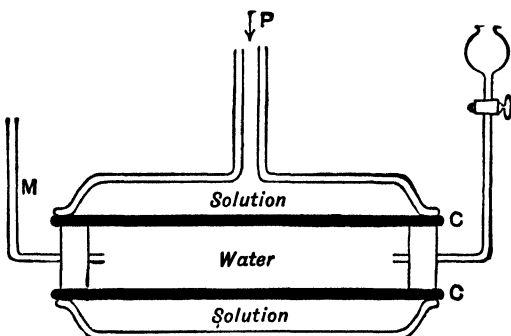


FIG. 116.—Apparatus of Berkeley and Hartley (diagrammatic).

two pressures are equal when no water passes through the membrane, the meniscus in *M* remaining stationary. The membrane is subjected to equal pressures on both sides and hence is less likely to fail under the high pressures measured. The osmotic pressures of solutions of moderate concentrations are very high and pressures over 100 atm. have been measured.

The laws of osmotic pressure.—The following results were obtained by Pfeffer with dilute solutions of cane sugar :

OSMOTIC PRESSURES OF SUGAR SOLUTIONS AT 0° C.

Concentration <i>C</i>	-	10.03	20.14	40.60	61.38 gm./lit.
Pressure <i>P</i>	-	0.686	1.34	2.75	4.04 atm.
Ratio <i>P/C</i>	-	0.068	0.067	0.068	0.066

The ratio is practically constant, hence *the osmotic pressure at a constant temperature is proportional to the concentration*. Let *V* = volume of solution containing 1 mol of solute (dissolved substance). Then $1/V = C$.
 $\therefore P/C = PV = \text{const.}$ This is the analogue of Boyle's law.

OSMOTIC PRESSURES OF 1 PER CENT. CANE SUGAR SOLUTIONS.

Absolute temp. <i>T</i> °	-	273	287.2	305.0
Pressure <i>P</i> (atm.)	-	0.648	0.671	0.716
Ratio <i>P/T</i> . 10 ³	-	2.37	2.33	2.35

The ratio is practically constant, hence *the osmotic pressure for a given concentration is proportional to the absolute temperature*, or $P = kT$. This is the analogue of Charles's law.

The mean value of *P/C* at 0° C. is 0.066 ; this is the osmotic pressure in atm. exerted by 1 gram of sugar in 1 litre of solution. Since the molecular weight of sugar is 342, this is also the pressure exerted by 1 gram molecule of sugar in 342 litres. The pressure is proportional to the concentration, hence it becomes 1 atm. when the volume containing 1 gram molecule (mol) is $342 \times 0.066 = 22.6$ litres. 1 mol of ideal gas confined in a space of 22.4 litres at 0° exerts a pressure of 1 atm. The value 22.6 for a molar solution is nearly 22.4, hence solutions obey Avogadro's law.

Van't Hoff * in 1886 summarised these results in the statement that dissolved substances obey the gas laws. *The osmotic pressure of a solution is equal to the gas pressure which the solute would exert if all the solvent were removed and the dissolved substance were left in the space in the condition of an ideal gas.*

* Van't Hoff's paper on " The Role of Osmotic Pressure in the Analogy between Solutions and Gases " is translated in *Alembic Club Reprint* No. 19.



FIG. 117.—J. H. VAN'T HOFF (1852-1911).

This is only approximate but becomes more exact in dilute solutions just as the gas laws are exact only at small pressures.

At 0° a sugar solution containing 1 gm./lit. has an osmotic pressure of 0.066 atm. $= 0.066 \times 76 \times 13.6$ gm. per sq. cm. The volume containing 1 mol is 342,000 c.c. The absolute temperature is 273. Hence in the general gas equation (p. 84)

$$PV = RT$$

we have :

$$0.066 \times 76 \times 13.6 \times 342,000 = R \times 273.$$

$\therefore R = 85,410$ gm. cm./ 1° , which is approximately the same as the value for a gas, viz. 84,780.

Isotonic solutions.—An ingenious method of *comparing* the osmotic pressures of solutions was discovered by de Vries in 1884. He observed under the microscope that the protoplasm content of living plant cells contracts in a concentrated salt solution. This is called **plasmolysis**. The thin outer wall of the protoplasm acts as a semipermeable membrane and when the osmotic pressure of the solution outside is greater

than that of the natural solution inside, water is forced out of the protoplasm and it shrinks from the rigid cell wall. If the osmotic pressure outside is less than that inside, the protoplasm takes up water and swells, and when the pressures are equal there is no effect on the cell protoplasm. Hence it is possible to make up a number of solutions all having the same osmotic pressure as the cell content, and these solutions must themselves have equal osmotic pressures. These are called **isotonic solutions** and it is found that they contain amounts of dissolved substances in the ratio of the molecular weights when they are non-electrolytes, but in the case of electrolytes the isotonic solutions contain equal numbers of particles (ions + molecules) in equal volumes.

Freezing points of solutions.—Bishop Watson in 1771 and Blagden in 1788 found by experiments with solutions of salts in water that *the lowering of freezing point is proportional to the concentration*. This is usually called "Blagden's law". If the depression of freezing point of water by C mols of cane sugar per 1000 gm. of water is D° , the following experimental results show that D/C is constant :

C	D	D/C
0.000344	0.000645	1.87
0.002303	0.004332	1.88
0.01026	0.01906	1.86
0.01841	0.03434	1.87
0.0365	0.06793	1.86

Raoult* in 1883 found experimentally that *if quantities of different substances in the ratio of the molecular weights are dissolved in identical weights of a solvent, the freezing points of the solutions are identical*. A molecular weight in grams of a substance dissolved in 1 kilogram of water depresses the freezing point by 1.86° . This is called the **molecular depression of freezing point Δ** for water. The value of Δ varies from one solvent to another.

Let the depression of freezing point produced by w gm. of solute per kgm. of solvent be D . That produced by the molecular weight M in 1 kgm. is the molecular depression Δ . Further, the two depressions are in the ratio of the concentrations, hence :

$$\frac{D}{\Delta} = \frac{w}{M}$$

$$\therefore M = \frac{w\Delta}{D}.$$

* Raoult's papers are collected in the volumes "Détermination des poids moléculaires" and "La dissolution", in *Les classiques de la découverte scientifique* (Paris, Gauthier-Villars).

EXAMPLE.—1.35 gm. of carbon tetrachloride dissolved in 55 gm. of acetic acid depressed the freezing point from 16.750° to 16.132° . Find the molecular weight of carbon tetrachloride.

w = number of gm. of solute per 1000 gm. of solvent = $1.35 \times 1000/55$.

D = observed depression = $16.750 - 16.132 = 0.618^{\circ}$.

Δ = molecular depression for acetic acid = 3.9° .

Molecular weight of solute $M = \frac{w\Delta}{D} = \frac{1.35 \times 1000 \times 3.9}{55 \times 0.618} = 155$.

The molecular weight calculated from the formula CCl_4 is 153.

Determination of lowering of freezing point.—The apparatus used to find the depression of freezing point is shown in Fig. 118.

A very sensitive **Beckmann thermometer** D is used, which has a large bulb and only six degrees on the whole scale, the latter being graduated in hundredths of a degree. There is a reservoir at the top of the capillary tube into which mercury can be shaken if higher temperatures are used, or from which mercury can be drawn into the tube and bulb if lower temperatures are used. The actual readings on the scale do not matter, as only their *difference* is required.

About 20 gm. of the solvent are weighed into the tube A and a stirrer of bent wire and a thermometer are fitted into the tube through a cork, so that the bulb is covered with the liquid. The tube A is fitted through a cork into a large test-tube B , which serves as an air-jacket and prevents too rapid fall in temperature. The tube B is supported in a freezing mixture (*e.g.* ice and salt) contained in the large jar C .

The stirrers in the solvent tube and outer jar are worked, and the thermometer observed. The mercury falls steadily to a certain point, when the solvent is slightly supercooled. Freezing then commences, the temperature at once runs up to the freezing point, and afterwards remains stationary. It is then read off with a lens, the thermometer being gently tapped to prevent any adhesion of mercury to the glass. Suppose the reading is 3.216° (thousandths of the degree are estimated).

The tube A is then taken out and allowed to warm till the solvent liquefies. A weighed quantity of the substance is introduced through the side tube and dissolved by working the stirrer. The tube is replaced in the air-jacket and put into the freezing mixture. The process is carried out as with the pure solvent, and the freezing point of the solution read

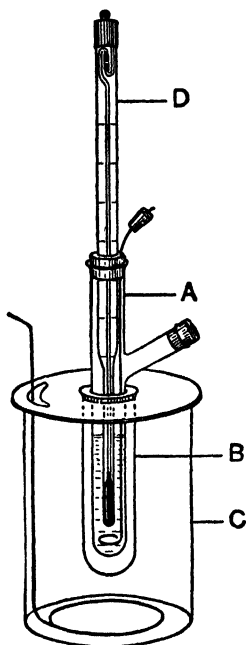


FIG. 118.—Beckmann's freezing point apparatus.

off. Suppose this to be 2.839° ; then D , the depression of freezing point, is $3.216 - 2.839 = 0.377^{\circ}$.

Eutectic mixtures.—When a salt solution freezes only pure ice generally separates and thus the remaining solution becomes more concentrated. Freezing, like distillation, will separate the components of a solution. If the freezing is continued the solution becomes richer and richer in salt and the freezing point lower and lower, since the more concentrated the solution the lower is the freezing point. This cannot go on indefinitely because a point is reached when the water left in the solution is only just sufficient to dissolve the salt.

On further cooling, both ice and salt must separate together in the same ratio as they exist in the solution; hence the temperature becomes constant and the whole of the solution solidifies without further fall in temperature. This minimum temperature was formerly called the *cryohydric temperature* and the mechanical mixture of ice and solid salt separating was supposed to be a compound, and called a *cryohydrate* (Guthrie, 1875). Later experiments showed by microscopic examination and in other ways that the supposed cryohydrates are mechanical mixtures and they are now known as *eutectic mixtures*, the lowest temperature attainable on freezing the solution being called the *eutectic temperature*.

The process may be represented graphically, but it is more convenient to take as an example a mixture of metals. Fig. 119 shows the freezing-point curves for mixtures of lead and antimony. The freezing point of pure

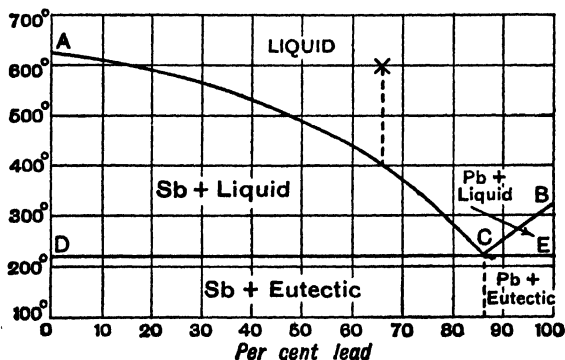


FIG. 119.—Freezing-point curves for antimony and lead,

antimony at A is 630.5° , that of pure lead at B is 327.4° . Addition of lead to fused antimony lowers the freezing point progressively along AC till the eutectic point C is reached. In the region ACD solid antimony is in equilibrium with liquid alloys. Addition of antimony to fused lead lowers the freezing point along BC till the eutectic point C is reached. In the region BCE solid lead is in equilibrium with liquid alloys. At C solid lead and solid antimony are in equilibrium with one liquid alloy of the composition of the eutectic mixture. Below DE all is solid.

Boiling points of solutions.—When a substance is dissolved in a solvent the boiling point of the solvent is raised. Raoult found that (i) *the elevation of boiling point is proportional to the concentration*, (ii) *the molecular elevation of boiling point is constant for a given solvent*.

If w gm. of substance in 1 kgm. of solvent raise the boiling point by D° , then if M is the molecular weight of the dissolved substance we have $D/E = w/M$, where E is the molecular elevation of boiling point, *i.e.* the rise in boiling point for 1 mol of non-volatile solute in 1 kgm. of solvent. Hence

$$M = \frac{wE}{D}.$$

In some types of apparatus, as in that described below, the molecular elevation is referred to the *volume* of the solution, and in that case E is the elevation produced by 1 mol in 1 litre of solution at the boiling point. The two values of E are different.

McCoy's apparatus consists of an outer tube A containing some of the solvent and an inner tube B which is graduated as shown and is fitted with a Beckmann thermometer (Fig. 120). About 15 c.c. of solvent are put into B and the solvent in A is boiled, the clip c being closed. The vapour from A passes into B through the inner tube ab , which is open to the vapour in A at a and ends in a perforated bulb at b . The vapour condenses and raises the solvent in B to the boiling point, a slow distillation taking place through the condenser C . The boiling point of the solvent is read off. The clip c is now opened (to prevent liquid being drawn back from B into A) and the boiling stopped. A weighed amount of the substance is now added to B by taking out the cork and thermometer, which are then replaced. The clip c is closed and the liquid in A again boiled. The vapour condenses in the solution in B and raises it to the boiling point of the resulting solution. When the temperature is steady the clip c is again opened, the thermometer is taken out and the volume of the solution in B is read. The fact that B is enclosed in a vapour jacket makes the amount of condensation necessary to raise the solution to its boiling point relatively small.

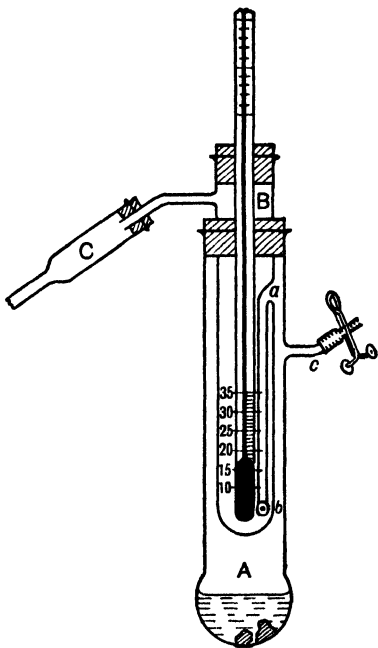


FIG. 120.—McCoy's boiling point apparatus.

EXAMPLE.—1.710 gm. of urea gave 28.6 c.c. of solution in water, boiling at 100.557°. The molecular elevation is 0.540°. Find the molecular weight.

$$\begin{aligned} w &= 1.710 \times 1000 / 28.6 &= 59.79. \\ \text{Observed elevation of boiling point} &= 0.557^\circ = D. \\ \text{Molecular elevation} &= 0.540^\circ = E. \\ \therefore M = wE/D &= 0.540 \times 59.79 / 0.557 = 58 \text{ (CON}_2\text{H}_4 = 60). \end{aligned}$$

Vapour pressures of solutions.—The vapour pressure of a solution of a non-volatile solute is smaller at any given temperature than the vapour pressure of the pure solvent. If p_0 is the vapour pressure of the pure solvent, p that of the solution, then the relative lowering of vapour pressure is the ratio $\frac{p_0 - p}{p_0}$. This is found to be (1) *proportional to the concentration of the solution*; (2) *practically independent of temperature within certain limits*; (3) *the same for equimolecular amounts of different substances in identical weights of a solvent*; (4) *the same for different solvents when the ratio of the number of mols of solute to the total number of mols (solute plus solvent) is the same* (Raoult, 1887).

The molecular lowering of vapour pressure is therefore a constant for a given solvent. In a solution containing N gm. mol. of solvent and n gm. mol. of solute, the relative lowering of vapour pressure is :

$$(p_0 - p)/p_0 = n/(N + n).$$

For 1 mol of solute dissolved in 99 mols of solvent the lowering of vapour pressure will be 1 per cent., since

$$n/(N + n) = 1/(99 + 1) = 0.01.$$

The value of N is calculated from the weight of solvent divided by its molecular weight in the state of *vapour*.

EXAMPLE.—Pure benzene, C_6H_6 , has a vapour pressure of 751.86 mm. at 80°. When 2.47 gm. of ethyl benzoate are dissolved in 100 gm. of benzene, the solution has a vapour pressure of 742.6 mm. at 80°. The molecular weight of benzene vapour is 78. $N = 100/78 = 1.282$;

$$(p_0 - p)/p_0 = (751.86 - 742.6)/751.86 = 0.0123;$$

$\therefore 0.0123 = n/(1.282 + n)$; $\therefore n = 0.01598$. But $n = 2.47/(\text{mol. wt. of ethyl benzoate})$; $\therefore \text{mol. wt. of ethyl benzoate} = 2.47/0.01598 = 154.5$. That calculated from the formula $\text{C}_6\text{H}_5\cdot\text{COO}\cdot\text{C}_2\text{H}_5$ is 150.

The lowering of vapour pressure and hence the elevation of boiling point are connected with the lowering of freezing point as is seen from the curves of Fig. 121. OA is the vapour pressure curve of the pure solvent.

At the freezing point t_0 , this cuts the vapour pressure (sublimation) curve of ice OB , which has a different slope (exaggerated in the figure). The vapour pressure curve of the solution $O'A'$ lies below that of the solvent and cuts the ice curve at O' , which is the freezing point t of the solution, when ice and solution are in equilibrium.

For small depressions OB and $O'O''$ may be taken as straight lines, and hence OO'' is proportional to $O'O''$, i.e. to $t_0 - t$. Hence the lowering of vapour pressure is proportional to the depression of freezing point.

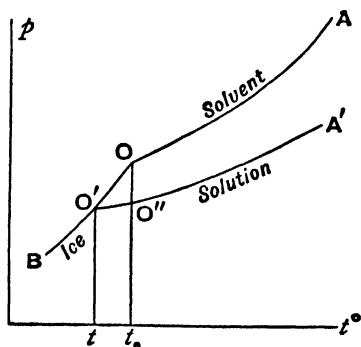


FIG. 121.—Vapour pressure curves of solvent, solution and ice.

It should be noted that the laws of depression of freezing point, elevation of boiling point and lowering of vapour pressure given are true only when the *pure* solvent separates from the solution as solid or vapour, and no solute separates.

Deliquescence.—The lowering of vapour pressure of water by a dissolved substance explains **deliquescence**, which is the liquefaction of very soluble substances such as calcium chloride, ferric chloride and caustic soda on exposure to moist air. Atmospheric moisture is attracted and a little *saturated* solution is formed. Since this is very concentrated its vapour pressure is less than the partial pressure of water vapour in the atmosphere. The solution goes on absorbing water vapour and since when it is diluted more solid dissolves, in the end all the solid will go into solution.

Electrolytes.—In solutions of electrolytes the osmotic pressure, depression of freezing point and elevation of boiling point are all abnormal. They are all proportional to the total number of solute particles in a given volume and if the solute is dissociated into ions it produces a larger number of particles, and hence a greater effect for a given mass, than if it were not ionised. A smaller quantity than 1 mol will thus produce the same effect as 1 mol of a normal (un-ionised) substance.

If the observed osmotic pressure is P' and the observed depression of freezing point or elevation of boiling point is D' , whilst the normal values are P and D , then the ratio P'/P or D'/D (which are equal to one another) is called *van't Hoff's factor* and denoted by i .

If electrolytes obeyed the same laws as non-electrolytes, the degree of ionisation could be calculated from van't Hoff's factor $i = \text{observed osmotic pressure} / \text{ideal osmotic pressure}$. Let α = degree of ionisation and let n

ions be formed from 1 molecule of electrolyte on complete ionisation. Then in the solution each mol of dissolved electrolyte gives :

$(1-x)$ mols of undissociated electrolyte,

nx mols of ions,

or $1 + (n-1)x$ mols of solute in all.

$$\text{Hence} \quad \frac{P'}{P} = \frac{D'}{D} = i = \frac{1 + (n-1)x}{1}.$$

$$\therefore x = (i-1)/(n-1),$$

from which x can be calculated.

EXAMPLE.—A solution of 4.98 gm. of cadmium iodide in 100 gm. of water freezes at -0.320° . The mol. wt. of CdI_2 is 366 ; \therefore the solution contains $49.8/366 = 0.136$ mols per 1000 gm. of water. If the salt were undissociated this would produce a freezing point depression of $0.136 \times 1.858^\circ$ ($1.858^\circ = \text{molar depression, p. 214}$). The observed depression is 0.320° .

$$\therefore i = 0.320/(0.136 \times 1.858) = 1.266.$$

If the dissociation equation is $\text{CdI}_2 = \text{Cd}^{++} + 2\text{I}^-$, $n = 3$;

$$\therefore x = (i-1)/(n-1) = 0.266/2 = 0.133,$$

i.e. 13.3 per cent. of the cadmium iodide is ionised.

In the case of *strong electrolytes*, which are largely ionised ($x > 0.9$), this method does not give accurate results. Such electrolytes are now regarded as practically completely ionised in dilute solutions (see p. 207) and the value of x calculated from i has no significance, although i itself still retains its *experimental* meaning.

Colloids.—Thomas Graham in 1849 found that some substances diffuse in water fairly rapidly and others very slowly. Salts, acids and bases are rapidly-diffusing substances; gum, gelatin and albumin (white of egg) diffuse *very* slowly. The rapidly diffusing substances, mostly crystalline in the solid state, were called **crystalloids** by Graham. Gum and albumin, which form amorphous solid masses resembling glue, were called **colloids** (Greek, *kolla*, glue). The differences were so great that Graham spoke of "two worlds of matter", the crystalloid and the colloid, each with characteristic properties.

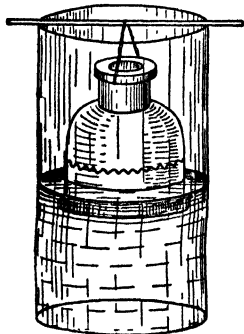


FIG. 122.—Graham's dialyser.

Dialysis.—Diffusion also occurs through membranes. A solution of potassium iodide and starch is poured into a **dialyser** (Fig. 122) consisting of a piece of parchment paper tied tightly over the mouth of a bell-jar. The dialyser is supported with the parchment paper dipping into distilled water in a jar. After half an hour chlorine water is added to the water in the jar; a yellow colour, due to liberated iodine, shows that the iodide has diffused through the parchment paper but the starch is retained, since this would have given a blue colour with the iodine (as may be seen by adding chlorine water to the liquid in the bell-jar).

Dispersed systems.—The *sharp* differentiation between crystalloids and colloids made by Graham, although it is of practical significance, is not true in general. Albumin may be obtained in a crystalline form and colloidal solutions of crystalline substances such as common salt may be prepared by precipitation in liquids (*e.g.* ether) in which they do not form true solutions. The real factor determining whether a substance forms a colloidal solution or a true solution is *the size of the dispersed particles*; as Graham suspected it is more correct to speak of the “colloidal state” of a substance than of a “colloidal substance”.

Colloidal solutions all contain particles which are larger than molecules and often much larger, but usually not microscopically visible. They float in a medium and do not tend to settle. Colloids are for this reason sometimes called **dispersed systems**. The commonest types of colloids are those containing minute solid or liquid particles suspended in a liquid medium, but other types of dispersed systems may also be formed.

Fogs and smokes are dispersed systems of liquid droplets and of solid particles respectively, in a gas. Smoke from the glowing tip of a cigarette, consisting of small particles of carbon, appears blue because the particles are very fine, with diameters of the order of a wave-length of light. Smoke some distance from the end of a cigarette, or blown from the mouth, appears greyish-white and opaque, because the particles are larger, probably as a result of the condensation of moisture upon them.

The Tyndall effect.—Very fine dust particles (“motes”) are visible in strong light, and the *ultramicroscopic* particles in colloidal solutions may be recognised by the **Tyndall effect**, *i.e.* the *scattering of light by small particles* (Fig. 123); the particles then appear much larger than they really are. A strong beam of light is sent through a colloidal



FIG. 123.—Tyndall cone.

solution, and on looking down on the path of the beam with a microscope, the colloid particles, which cannot be seen at all by light transmitted *through* the solution, become visible as bright points

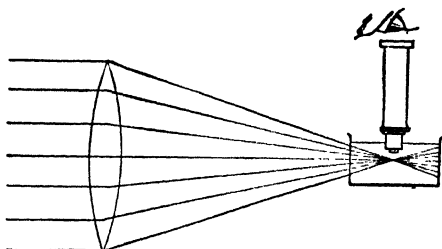


FIG. 124.—Diagram of ultramicroscope.

owing to their scattering effect. *The light scattered by colloid particles is polarised.* The apparatus is called an **ultramicroscope** (Fig. 124). The bright points when the particles are small enough have a zig-zag tremulous motion called the **Brownian movement** (dis-

covered by the English botanist, Robert Brown, in 1827).

The Brownian movement was explained by C. Wiener in 1863 as follows. The colloidal particle is bombarded on all sides by molecules of liquid striking against it. If the particle were very large, the effect would be uniform all over the surface, but if the particle is small there may be more molecules colliding on one side of it at a given instant than on the opposite side. The particle is therefore urged through the liquid by this unbalanced pressure until the unequal distribution of pressure shifts round and the particle starts off in another direction.

Electrophoresis.—Colloid particles often have an *electrical charge*, some positive and others negative. Such charged colloid particles move in an electrical field and this is called **electrophoresis** or **cataphoresis**.

Electrophoresis is shown by taking about 50 c.c. of colloidal arsenious sulphide (see below) and adding about 5 gm. of pure urea to make it denser than water. The yellow solution is then carefully run by a pipette into the lower part of a U-tube half-filled with distilled water. Platinum electrodes are placed in each arm of the tube and connected with the D.C. mains. The level of arsenic sulphide, marked by paper rings, falls on one side of the U-tube and rises on the other (Fig. 125).

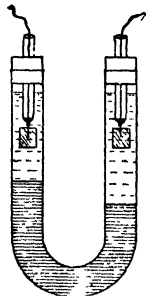


FIG. 125.—
Electrophoresis.

Precipitation of colloids by electrolytes.—If an electrolyte is added to a solution of a colloid which contains charged particles, one kind of ion of the electrolyte may neutralise the opposite charge on the colloid particles. The charges, on account of the repulsion, prevent the colloid particles from coming together, and when they are neutralised the colloid particles collect into large aggregates, which then precipitate from the solution. Negative

colloids such as arsenious sulphide are precipitated by positive ions, and positive colloids such as ferric hydroxide are precipitated by negative ions.

Ions with higher charges are more effective in precipitating (or coagulating) colloids. The cations are increasingly effective in the order $Al^{+++} > Ca^{++} > K^{+}$ in precipitating negative colloids, and the anions in the order $SO_4^{--} > Cl^{-}$ in precipitating positive colloids. This is called the *Schulze and Hardy rule*. Colloids of opposite charge, such as arsenious sulphide and ferric hydroxide, also mutually precipitate each other.

The lowest concentration of an ion which causes precipitation is called the **threshold concentration**. It may be determined as follows. Solutions of $N/2$ sodium chloride and $M/10$ (tenth molar) barium chloride and aluminium chloride are prepared. Mixtures of $N/2$ NaCl and distilled water are prepared in four test-tubes as follows :

ml. $N/2$ NaCl	9	5	2.5	1
ml. water	0	4	6.5	8

To each tube 1 ml. of arsenious sulphide sol is added and the contents well mixed. Each tube is examined for precipitation after 1 minute.

Since $BaCl_2$ and $AlCl_3$ are more active, 1 ml. of $M/10$ solution is mixed with 9 ml. of distilled water in one tube. Then 1 ml. of this $M/100$ solution is mixed with 9 ml. of water in a second tube to form $M/1000$ solution, and the dilution similarly continued in the third and fourth tubes. Then 1 ml. of the sol is added as before.

The experiments may be repeated with the positive ferric hydroxide sol using $M/10$ solutions of NaCl and Na_2SO_4 to examine the effect of the ions Cl^{-} and SO_4^{--} . This sol is very sensitive to OH^{-} ions, in spite of the low charge, since they remove hydrogen and ferric ions which stabilise the ferric hydroxide particles.

Colloidal solutions are often protected from precipitation by electrolytes by adding small amounts of colloids like gelatin, which are hence called **protective colloids**. Colloidal gold with very fine particles is ruby-red in colour, but traces of electrolytes cause the particles to aggregate to larger particles, when the solution becomes blue, and finally the particles may precipitate. The ruby-red gold solution is much more stable (as Faraday discovered) if a little gelatin solution is added.

Classification of colloids.—Colloidal solutions were formerly divided into *suspensoids* containing solid particles and *emulsoids* containing liquid particles, but a more satisfactory classification is into **lyophobic colloids** (solvent repelling) and **lyophilic colloids** (solvent attracting) according as they are, or are not, easily precipitated by electrolytes. This corresponds roughly to the old division into suspensoids and emulsoids. Lyophobic colloids have viscosities nearly the same as that of the solvent whilst lyophilic colloids (*e.g.* albumin, gum) are very viscous. The distinction between **sols** and **gels** is obvious.

The *surface* exposed by colloid particles is very large for a given weight. A cube of solid with 1 cm. edges exposes a surface of 6 sq. cm. When subdivided into eight cubes of edge 0.5 cm. the surface is 12 sq. cm., and if the subdivision is carried on until the parts are as small as the particles in colloidal solutions, the area exposed is about six and a half acres.

The particles have diameters between 1 and 100 millimicrons, a millimicron ($m\mu$) being one millionth of a millimetre. Particles larger than 100 $m\mu$ are microscopically visible and occur in suspensions; particles smaller than 1 $m\mu$ are not visible even with the ultramicroscope, and we are then in the region of true solutions.

Preparation of colloids.—Colloidal solutions of many metals may be obtained by striking electric arcs between two wires of the metal, for example platinum, under water. (A suitable resistance must be put in series to avoid blowing a fuse.) Very minute particles of the metal are dispersed through the water to form a colloidal solution. In other cases (*e.g.* copper, silver and lead) a salt of the metal is reduced in presence of a protective colloid.

Colloidal silica is prepared by adding a solution of sodium silicate to dilute hydrochloric acid and dialysing (p. 220). Colloidal arsenious sulphide is obtained as a yellow solution by pouring a solution of arsenious oxide in distilled water into a solution of hydrogen sulphide and removing the excess of hydrogen sulphide by a stream of washed hydrogen. It is a clear yellow solution but shows a Tyndall cone. Colloidal ferric hydroxide is prepared as a clear reddish-brown solution (also showing a Tyndall cone) by pouring a few c.c. of 30 per cent. ferric chloride solution into 500 c.c. of boiling distilled water, and dialysing. Arsenious sulphide particles are negatively charged, ferric hydroxide particles are positively charged.*

* Further information on colloids and accounts of experiments suitable for school laboratories will be found in E. Hatschek's *An Introduction to the Physics and Chemistry of Colloids* and *Laboratory Manual of Elementary Colloid Chemistry*.

CHAPTER XIX

CHEMICAL EQUILIBRIUM AND THE LAW OF MASS ACTION

Historical.—Albertus Magnus assumed that substances closely related to one another (*e.g.* mercury and gold) show the greatest tendency to combine, and he gave the name **affinity** (from *affinis*, related) to the cause of chemical combination. When the mutual action of acids and alkalis was examined it became clear that it is often *dissimilar* substances which enter most easily into reaction.

Boyle in his *Sceptical Chymist* (1661) observes that :

“notwithstanding, the particles of some bodies are so closely united, yet there are some which may meet with particles of other denomination, which are disposed to be more closely united with some of them than they are amongst themselves.” In this the *elective* character of chemical affinity is clearly expressed.

Mayow (1674) held very clear views on chemical affinity. If ammonia, he says, be added to hydrochloric acid, sal ammoniac is produced, in which neither acid nor alkaline properties are found. But if this is heated with potash, the ammonia is displaced, “because the acid is capable of entering into closer union” with potash than with ammonia. To show that an acid is not destroyed on neutralisation he refers to the distillation of nitre with sulphuric acid, which displaces the nitric acid and leaves in the retort the same substance as is produced by the direct action of sulphuric acid on potash; the nitric acid comes off “because the volatile acid . . . has been expelled from the society of the alkaline salt by the more fixed vitriolic acid”.

The idea that affinities were attractive forces was introduced by Newton, who in his *Opticks* (1717) says potash becomes moist because it attracts water from the air. Mercury precipitates silver, copper precipitates mercury, and iron precipitates copper, from solutions of salts because of the increasing attraction of the metals in this order for the acid.

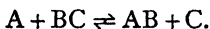
Geoffroy in 1718 and Bergman in 1775 generalised the results and said that if a substance A has a stronger attraction for another substance B than a third substance C has, then A will decompose BC *completely*,

turning out C and forming AB. Tables of affinity were drawn up giving the order in which acids, for example, displaced each other both in solution and in the state of fusion.

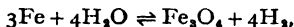
This theory of "elective affinities" was questioned by Berthollet (*Researches into the Laws of Affinity*, Cairo, 1799). He pointed out that the reaction $A + BC = AB + C$ does not always proceed to completion in one direction as it should according to Bergman's theory. It may proceed in the opposite direction under different conditions, and in general is not complete:

"in opposing the body A to the combination BC, the combination AB can never take place [completely], but the body B will be divided between the bodies A and C proportionally to the affinity and the quantity of each."

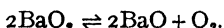
A state of equilibrium is then reached when two opposing reversible reactions balance each other, *i.e.* proceed with equal speeds. This is denoted by:



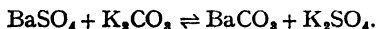
Examples of such reversible reactions are the action of steam on red-hot iron (p. 129):



and the Brin process (p. 116):



Dulong in 1813 found that if barium sulphate is boiled with successive quantities of concentrated potassium carbonate solution it is completely converted into barium carbonate; whilst barium carbonate when boiled with potassium sulphate solution is entirely transformed into barium sulphate:



The equilibrium state.—A state of equilibrium reached by the balancing of two opposing reactions is the same no matter which of the two groups of substances separated by the sign \rightleftharpoons we bring together in the first instance. Lemoine in 1877 proved that the same state of equilibrium is reached on heating hydrogen iodide at 444° for a sufficient time as on heating a mixture of hydrogen and iodine vapour in equivalent proportions at the same temperature: $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$.

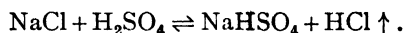
This shows that both reactions can go on *under the same conditions*; in the equilibrium state both are still proceeding, but the amount of hydrogen iodide formed in any instant is exactly equal to the amount decomposed. The two reactions are balanced, and the equilibrium is *dynamic*, not static.

A liquid comes into equilibrium with its vapour in a closed vessel when as many molecules leave the liquid as return to it in a given time. A salt is in equilibrium with its saturated solution when as many molecules

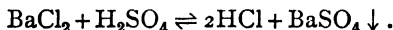
break away from the solid per second as are caught up again from the solution by the crystal. Barium peroxide heated in a closed vessel at a constant temperature breaks up into baryta and oxygen, and the baryta and oxygen recombine to form barium peroxide. A state of equilibrium is therefore set up at a definite pressure of oxygen, called the **dissociation pressure** : $2\text{BaO}_2 \rightleftharpoons 2\text{BaO} + \text{O}_2$.

Effect of volatility or insolubility of a product of reaction.—In many cases a reaction seems to go to completion instead of to a state of equilibrium. Berthollet said that this is often due to some *disturbance of the equilibrium state when some of the products of the reaction are removed from the sphere of action by their volatility or insolubility*. As soon as they leave the system by passing into the gaseous state or depositing as solids, they cease to exert any influence and the reaction by which they are produced, being no longer opposed, cannot become balanced and goes on until the change becomes nearly if not quite complete.

The effect of volatility had been noted by Mayow (p. 225) ; when a gas is evolved the equilibrium is disturbed and the reaction goes almost to completion :



If an insoluble precipitate is formed the same effect is produced :



Investigation of equilibrium states.—These examples show that in examining the amounts of substances existing in equilibrium the reverse reaction must not take place when the conditions are changed. If hydrogen iodide is heated until equilibrium is reached the proportions of HI, H₂ and I₂ may be found after *rapidly* cooling the mixture, when very little reaction occurs. In some cases, *e.g.* the dissociation of steam : $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$, this cooling must be performed exceedingly quickly, otherwise the reverse reaction occurs and no trace of the products of dissociation can be discovered.

Grove in 1847 heated a platinum wire in steam by an electric current. In contact with the hot wire dissociation occurs and the products at once pass into the diluting atmosphere of steam, which prevents recombination by separating them and by cooling.

Deville in 1864 proved the dissociation of gases at high temperatures with the apparatus shown in Fig. 126.

A wide tube of glazed porcelain with a narrower tube of unglazed porcelain supported axially inside was heated strongly in a furnace. Water vapour was passed through the inner tube and carbon dioxide through the annular space, and the gases from both were collected over potash solution, which absorbed the carbon dioxide. The steam was dissociated and hydrogen passed by diffusion through the porous tube

into the annular space, leaving most of the oxygen in the inner tube. If the two gases were passed to the same receiver, 1 c.c. of detonating gas ($2\text{H}_2 + \text{O}_2$) was collected for every gram of water passed through the apparatus. If carbon dioxide was passed rapidly through a glazed

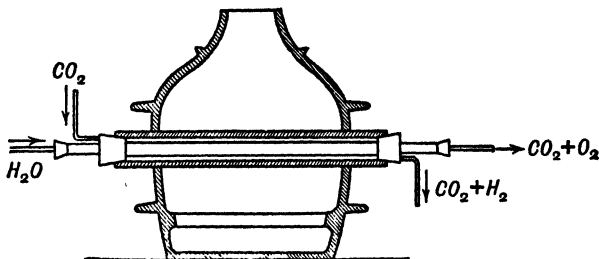


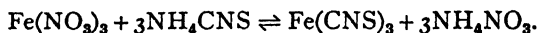
FIG. 126.—Deville's experiment on dissociation.

porcelain tube packed with fragments of porcelain strongly heated in a furnace dissociation occurred, and when the gas was collected over caustic potash, a small volume of a mixture of carbon monoxide and oxygen was obtained: $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$.

The law of mass action.—Berthollet not only proved the reversibility of reactions but also showed that *an excess of a substance may have an important influence on a reaction*. He called this the "effect of quantity" (see p. 226) or the "action of mass". This effect was expressed quantitatively by Guldberg and Waage* in 1864–7 as the **law of mass action**: *in reversible reactions, the extent of chemical change is proportional to the active masses of the interacting substances*.

If to a system of substances in equilibrium an excess of one reacting substance is added, then change occurs in such a way that the concentration of that substance is diminished.

This may be illustrated by an experiment due to J. H. Gladstone (1855). Ferric nitrate and ammonium thiocyanate react in solution to produce ferric thiocyanate which has a blood-red colour. The reaction is reversible:



If an excess of ferric nitrate or ammonium thiocyanate is added the intensity of the colour deepens, but if ammonium nitrate is added the colour becomes paler.

Prepare two solutions containing 3.5 gm. of crystallised $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 2.3 gm. of NH_4CNS in 1 litre of water, respectively. Mix 25 c.c. of each. A dark-red solution of $\text{Fe}(\text{CNS})_3$ is formed. Add 25 c.c. of this solution to 1 litre of water in each of four glass cylinders; a pale brownish-

* Pronounced *Vä-ga*.

red colour is produced. Keep one jar for reference and to the other three add : (a) 25 c.c. of the ferric nitrate solution, (b) 25 c.c. of the thiocyanate solution, (c) 25 c.c. of a saturated solution of NH_4NO_3 . Observe the colour change in each case.

Guldberg and Waage's deduction of the law of mass action was on the following lines.*

Consider the formation of hydrogen iodide from hydrogen and gaseous iodine. Molecules of HI can be formed only as the result of collisions of iodine and hydrogen molecules, the number of collisions per second being proportional to the number of molecules of each gas present in unit volume, *i.e.* to its *concentration*. The concentration may be denoted by the symbol enclosed in square brackets, *e.g.* $[\text{H}_2] = 0.1$ means 0.1 *mol* of hydrogen per *litre*.

The rate of reaction is therefore proportional to the *product* of the concentrations, $k_1[\text{H}_2] \times [\text{I}_2]$.

Similarly, the rate of decomposition of HI will be $k_2[\text{HI}]^2$, since *two* HI molecules must collide and the probability for this is proportional to $[\text{HI}]^2$. Hence :

$$\begin{aligned} &\text{rate of formation of HI} \\ &= \text{rate of combination of } \text{H}_2 \text{ and } \text{I}_2 - \text{rate of decomposition of HI} \\ &= k_1[\text{H}_2][\text{I}_2] - k_2[\text{HI}]^2. \end{aligned}$$

When the rate of formation of HI is zero the system is in equilibrium, since then HI is decomposed exactly as fast as it is formed and the amount of HI is independent of the time. Hence in equilibrium :

$$\begin{aligned} k_1[\text{H}_2][\text{I}_2] - k_2[\text{HI}]^2 &= 0 \\ \therefore k_1[\text{H}_2][\text{I}_2] &= k_2[\text{HI}]^2 \\ \therefore \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} &= \frac{k_1}{k_2} = K. \end{aligned}$$

At a given temperature K is constant ; it is called the *equilibrium constant*. It is independent of the amounts of iodine, hydrogen and hydrogen iodide originally taken but depends on the temperature.

The law of mass action holds for gases and also for *dilute solutions* (homogeneous systems), as was shown by van't Hoff in 1886.†

Examples of the applications of the law of mass action to substances in solution are given on pages 234 to 244.

In forming the equilibrium constant, it should be noted, the *products* of the reaction are put into the *numerator* of the ratio and each concentration

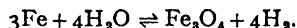
* The original is in French in *Études sur les affinités chimiques*, Christiania, 1867; German translation in Ostwald's *Klassiker* No. 104; there is no English translation.

† See the reference on p. 212.

is raised to the power n , where n is the number of molecules of the substance taking part in the reaction. The concentrations of the *initial substances* are in the *denominator*.*

Heterogeneous equilibria.—When *pure* solids take part in a reaction their vapour pressures or solubilities are constant at a given temperature, hence their concentrations are constant and may be included in the equilibrium constant K .

Consider the action of steam on red-hot iron :



In the gaseous phase, to which alone the law of mass action applies, we may consider that in addition to H_2O and H_2 at measurable and variable pressures, there are also present the vapours of the iron and oxide of iron at immeasurably small and constant pressures. In the mass action equation :

$$K' = \frac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4}$$

since $[\text{Fe}_3\text{O}_4]$ and $[\text{Fe}]$ are constant, we can write :

$$K' = \frac{[\text{Fe}_3\text{O}_4]}{[\text{Fe}]^3} \cdot \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} = k \cdot \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

or

$$K = \frac{[\text{H}_2]}{[\text{H}_2\text{O}]}$$

where

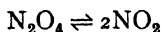
$$K = \sqrt[4]{K'/k}.$$

This shows that the ratio of the concentrations (or partial pressures) of hydrogen and steam is constant at a given temperature, and independent of the amounts of solid iron or iron oxide present.

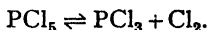
Le Chatelier's principle.—The effect of change of pressure or temperature on a system in equilibrium is qualitatively given by a principle enunciated by Le Chatelier † :

If a system in equilibrium is subjected to a constraint, a change occurs if possible of such a kind that the constraint is partly annulled.

(i) *Effect of change of pressure.*—Consider the dissociation of nitrogen peroxide gas :



or of phosphorus pentachloride vapour :



At a given temperature, if the pressure is increased a reaction will occur which tends to diminish the pressure, *i.e.* 2NO_2 will combine to form

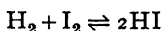
* This convention is now generally used.

† Pronounced *Chât-éliér*, not *Châ-téliér*.

N_2O_4 , and PCl_3 and Cl_2 will combine to form PCl_5 . It is important to notice that in this case *the equilibrium constant K is not altered by the change of pressure*, since it depends only on temperature for a given chemical reaction. The values of

$$[\text{NO}_2]^2/[\text{N}_2\text{O}_4] \text{ and } [\text{PCl}_3][\text{Cl}_2]/[\text{PCl}_5]$$

remain the same. If the reaction occurs without change of volume, *e.g.*



then change of pressure has no effect on the equilibrium.

This may be shown by supposing the concentrations increased n times by an n -fold increase of pressure. In the case of hydrogen iodide the concentration product is

$$\frac{n[\text{H}_2] \cdot n[\text{I}_2]}{(n \cdot [\text{HI}])^2} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = K,$$

i.e. the mixture is still in equilibrium. In the case of PCl_5

$$\frac{n[\text{PCl}_3]n[\text{Cl}_2]}{n[\text{PCl}_5]} = \frac{n[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]},$$

i.e. the product is n times as large as the equilibrium value, and some combination of PCl_3 and Cl_2 to form PCl_5 must occur until the equilibrium value is restored.

(ii) *Effect of change of temperature.*—Le Chatelier's principle shows that *if the temperature of a system in equilibrium is raised (or lowered) that one of the two reversible reactions will occur which absorbs (or evolves) heat*. The dissociation of PCl_5 increases with rise in temperature, because the reaction $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ absorbs heat.

There are three points which must be carefully attended to in the application of Le Chatelier's principle in the case of temperature effects :

- (i) it applies only to systems in true equilibrium ;
- (ii) it has nothing to do with velocity of reaction ;
- (iii) the equilibrium *constant* is usually changed.

Nearly all reactions increase in velocity with rise in temperature, the velocity being roughly doubled for a rise of 10° , so that the rate increases very rapidly with temperature.

Ozone is formed from oxygen, $3\text{O}_2 = 2\text{O}_3$, with absorption of heat. At very high temperatures oxygen and ozone can be in equilibrium, and ozone is known to be formed from oxygen at very high temperatures, *e.g.* in flames. At the ordinary temperature ozone should practically not exist at all, since the equilibrium is almost completely on the oxygen side. Ozone exists because it is *metastable*, *i.e.* if it is decomposing into oxygen the rate is so slow that the change is hardly noticeable. When ozone is heated to about 300° , however, it decomposes rapidly, because the velocity of change into oxygen is increased so as to be very appreciable. At moderate temperatures ozone can exist *in equilibrium* with oxygen only in small

traces, so that although it actually becomes more stable in the equilibrium state at higher temperatures, the increase in the velocity of change from the metastable state of ozone to the stable state of oxygen quite outweighs the increase in stability of the ozone.

(iii) *Effect of addition of products of reaction.*—The effect of adding an excess of one of the products of reaction *at constant volume* is obvious from the law of mass action. In the case of the dissociation of hydrogen iodide

$$\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = K,$$

addition of excess of H_2 or I_2 vapour will cause an increase of $[\text{H}_2]$ or $[\text{I}_2]$, respectively (since V is constant), hence to maintain the value of K , $[\text{HI}]$ must also increase, *i.e.* the extent of dissociation is diminished. The same effect is produced by adding excess of Cl_2 or PCl_3 vapour to partly dissociated PCl_5 , since in this case

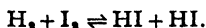
$$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = K,$$

and increase of $[\text{PCl}_3]$ or $[\text{Cl}_2]$ must be followed by an increase of $[\text{PCl}_5]$ in order to maintain K constant.

The effect of addition of products of reaction *at constant pressure* is not so obvious, but it can be shown by calculations based on the law of mass action that in both the above cases the dissociation is reduced when H_2 or I_2 is added to the first equilibrium mixture, and PCl_3 vapour or Cl_2 to the second, at constant total pressure.

Calculations of equilibria.—Three examples may be given of numerical calculations based on the application of the law of mass action to gaseous systems.*

EXAMPLE 1.—7.94 c.c. of hydrogen (at S.T.P.) and 0.0601 gm. of solid iodine were heated in a sealed bulb at 444° until equilibrium was reached :



9.52 c.c. of hydrogen iodide (at S.T.P.) were formed. Find the equilibrium constant. At S.T.P. 2×127 gm. of iodine (I_2) occupy 22,420 c.c. \therefore vol. of I_2 vapour at S.T.P. initially present

$$= \frac{22420 \times 0.0601}{2 \times 127} = 5.30 \text{ c.c.}$$

The 9.52 c.c. of HI are formed from 4.76 c.c. of H_2 and 4.76 c.c. of I_2 ; \therefore in equilibrium :

$$\text{vol. of } \text{H}_2 = 7.94 - 4.76 = 3.18 \text{ c.c.}$$

$$\text{vol. of } \text{I}_2 = 5.30 - 4.76 = 0.54 \text{ c.c.}$$

$$\text{vol. of HI} = 9.52.$$

* Examples of such calculations will be found in Partington and Stratton, *Intermediate Chemical Calculations*, Chapter X.

Hence if V is the volume of the bulb in litres the *concentrations* in mols per litre are: $[H_2] = 3.18/22420V$; $[I_2] = 0.54/22420V$; $[HI] = 9.52/22420V$;

$$\therefore K = \frac{[H_2] \times [I_2]}{[HI]^2} = \frac{3.18 \times 0.54}{(9.52)^2} = 0.01895.$$

EXAMPLE 2.—8.10 c.c. of hydrogen and 2.94 c.c. of iodine vapour (at s.t.p.) are heated at 444° . What volume of HI will be formed in equilibrium? Let $2x$ c.c. be formed:

$$\begin{array}{ccccccc} H_2 & + & I_2 & \rightleftharpoons & 2HI \\ \text{Volumes: } (8.10 - x) & & (2.94 - x) & & 2x \\ \therefore \frac{(8.10 - x)(2.94 - x)}{4x^2} & = & 0.01895. \end{array}$$

$\therefore x = 2.825$ or 9.12 . Only the root 2.83 is admissible, since 2.94 c.c. of I_2 vapour can give only 5.88 c.c. of HI as a maximum. Thus, the volume of HI formed $= 2 \times 2.83$ c.c. $= 5.66$ c.c. at s.t.p.

EXAMPLE 3.—2.0 gm. of PCl_5 are sealed in an evacuated bulb of 200 c.c. capacity and heated at 200° . Find the pressure developed if PCl_5 is 48.5 per cent. dissociated under 1 atm. pressure at 200° C.

2.0 gm. of $PCl_5 = 2.0/208 = 0.0096$ gm. mol. Let x = degree of dissociation under the conditions of experiment. 200 c.c. $= 0.2$ litre. The concentrations are:

$$\begin{aligned} [PCl_5] &= \frac{0.0096(1-x)}{0.2}; \quad [PCl_3] = [Cl_2] = \frac{0.0096x}{0.2}; \\ \therefore K &= \frac{0.0096x^2}{0.2(1-x)} \dots\dots\dots (i) \end{aligned}$$

At 200° under 1 atm. pressure PCl_5 is 48.5 per cent. dissociated. Hence $x = 0.485$ and $1-x = 0.515$. The volume of 1 gm. mol. under these conditions is:

$$22.4 \times 1.485 \times \frac{473}{273} = 57.6 \text{ litres.}$$

$$\text{Hence} \quad K = \frac{(0.485)^2}{0.515 \times 57.6} = 0.00793. \dots\dots\dots (ii)$$

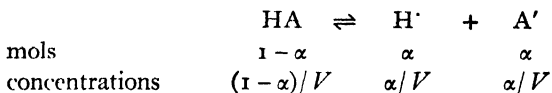
From the two expressions for K we find on solving the quadratic equation $x = 0.332$.

One gm. mol. of PCl_5 produces $1+x$ gm. mol. on dissociation, hence there are 1.332×0.0096 gm. mols. in 200 c.c. at 200° C. One mol in 1 litre exerts a pressure of 22.4 atm. at s.t.p., and the pressure will be

$$1.332 \times 0.0096 \times \frac{22.4}{0.2} \times \frac{473}{273} = 2.48 \text{ atm.}$$

The degree of dissociation falls from 0.485 to 0.332 when the pressure increases from 1 to 2.48 atm.

Ostwald's dilution law.—Let 1 gram molecule (1 mol) of a *weak* (i.e. slightly ionised) monobasic acid (such as acetic acid CH_3COOH) be dissolved in V litres of water, and let the degree of electrolytic dissociation of the acid at this dilution be α . The dissociation equilibrium can be represented by the equation :



Thus $[\text{HA}] = \frac{1 - \alpha}{V}$; $[\text{H}^+] = [\text{A}^-] = \frac{\alpha}{V}$,

and the equation of mass action is :

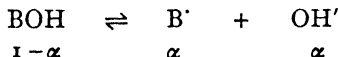
$$\frac{[\text{H}^+] \times [\text{A}^-]}{[\text{HA}]} = \text{const.} = K.$$

If we put $K = K_a$, the dissociation constant of the acid,

$$\frac{\alpha}{V} \cdot \frac{\alpha}{V} / \frac{1 - \alpha}{V} = \frac{\alpha^2}{(1 - \alpha)V} = K_a. \dots\dots\dots(1)$$

This is called Ostwald's Dilution Law.

A similar equation may be derived for the electrolytic dissociation of a *weak* monacid base, such as ammonium hydroxide, NH_4OH :

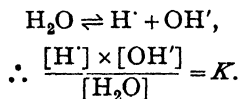


and if K_b is the dissociation constant of the base,

$$(1 - \alpha)V = K_b. \dots\dots\dots(2)$$

On account of the disturbing effect of the charged ions in solutions of strong electrolytes (largely ionised in solution), Ostwald's Dilution Law does not apply to them but only to weak acids and bases, which have small ionisations α and hence small dissociation constants K_a and K_b . *The law of mass action cannot be applied to strong electrolytes.*

The law of mass action may be applied to the ionisation of water :



Since the degree of ionisation of water is very small, $[\text{H}_2\text{O}]$ may be regarded as a constant and included in the equilibrium constant ; hence :

$$[\text{H}^+] \times [\text{OH}^-] = K[\text{H}_2\text{O}] = \text{const.} = K_w$$

where K_w is called the *ionic product* for water.

At room temperature, 18° , the value of K_w is approximately 10^{-14} , the concentrations being expressed in mols per litre. Since in pure water or in any neutral solution, $[H^+] = [OH^-]$, it follows that each concentration is 10^{-7} , since

$$K_w = [H^+] \times [OH^-] = 10^{-7} \times 10^{-7} = 10^{-14}. \dots\dots\dots(3)$$

The condition for neutrality is not that $[H^+]$ or $[OH^-]$ shall be zero, but that they shall be equal. They can be equal only when each is 10^{-7} , since their product must always be 10^{-14} . If either $[H^+]$ or $[OH^-]$ is known, the other can be found from equation (3).

Consider a centinormal ($N/100$) solution of a *strong* monobasic acid. At this dilution the acid is practically completely ionised. Hence

$$[H^+] = \frac{1}{100} = 10^{-2},$$

$$\therefore [OH^-] = \frac{[H^+] \times [OH^-]}{[H^+]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}.$$

This is the hydroxide ion concentration in the solution.

Similarly, in a $N/100$ solution of a *strong* alkali in which complete ionisation may be assumed,

$$[OH^-] = \frac{1}{100} = 10^{-2},$$

$$\therefore [H^+] = \frac{[H^+] \times [OH^-]}{[OH^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}.$$

This is the hydrogen ion concentration in the solution.

The pH scale.—Since in solutions of weak acids and bases to which the law of mass action applies the values of $[H^+]$ and $[OH^-]$ are very small, they will be represented by powers of 10 with large negative exponents. *E.g.*

$$[H^+] = 1.6 \times 10^{-8} = 10^{-7.8}.$$

These are inconvenient to write and another convention is now largely used, viz. the so-called **pH scale**. The exponent of the hydrogen ion concentration *with the sign changed* is called pH.

Thus, in a solution for which $[H^+] = 10^{-7.8}$ it is said that $\text{pH} = 7.8$. It is clear that pH is also the logarithm of the hydrogen ion concentration *with the sign changed*, since

$$\log 10^{-7.8} = -7.8,$$

$$\text{or} \quad \log 1.6 \times 10^{-8} = -8 + \log 1.6 = -8 + 0.20 = -7.8.$$

Since in neutral solutions $[H^+] = 10^{-7}$, such solutions have a $\text{pH} = 7$. pH increases as $[H^+]$ the hydrogen ion concentration decreases, large values of pH corresponding with small values of $[H^+]$ and *vice versa*. Increasing pH means that the solution is becoming less acid or more alkaline.

In $0.01N$ monobasic acid, assumed completely ionised :

$$[H^+] = 0.01 = 10^{-2}, \quad \therefore \text{pH} = 2.$$

In 0.01*N* alkali, assumed completely ionised :

$$[\text{OH}^-] = 0.01 = 10^{-2}.$$

$$\therefore [\text{H}^+] = \frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}, \quad \therefore \text{pH} = 12.$$

In 0.001*M* (molar) lime water, $\text{Ca}(\text{OH})_2$, assumed completely ionised,

$$[\text{OH}^-] = 0.002 = 2 \times 10^{-3} = 10^{-2.7},$$

$$\therefore [\text{H}^+] = \frac{10^{-14}}{10^{-2.7}} = 10^{-11.3}, \quad \therefore \text{pH} = 11.3.$$

Ionisations of weak acids and bases.—Ostwald's Dilution Law may be used to calculate the equilibrium constant for a *weak* acid or base when the degree of electrolytic dissociation for one dilution is known.

EXAMPLE 1.—At 18°, *N*/100 acetic acid has a degree of dissociation of 0.042.

$$\frac{\alpha^2}{(1 - \alpha)V} = K_a.$$

$$\alpha = 0.042. \quad \therefore 1 - \alpha = 0.958; \quad V = 100.$$

$$\therefore K_a = \frac{(0.042)^2}{0.958 \times 100} = 1.84 \times 10^{-6}.$$

Ostwald's Dilution Law may also be used to find the hydrogen ion concentration in a solution of given dilution of a *weak* acid of which the dissociation constant is known, or similarly the hydroxide ion concentration in a solution of a *weak* base.

EXAMPLE 2.—The dissociation constant of a weak monobasic acid at 18° is 6.2×10^{-6} . Calculate the hydrogen ion concentration in a *N*/100 solution of the acid.

$$\frac{\alpha^2}{(1 - \alpha)V} = 6.2 \times 10^{-6}.$$

Since the acid is weak, α is small and $1 - \alpha$ may be put equal to unity. Hence $\alpha^2/100 = 6.2 \times 10^{-6}$.

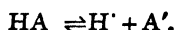
$$\therefore \alpha = \sqrt{62 \times 10^{-8}} = 7.9 \times 10^{-3}.$$

$$\text{But} \quad [\text{H}^+] = \frac{\alpha}{V} = \frac{7.9 \times 10^{-3}}{100} = 7.9 \times 10^{-5}.$$

If it is not permissible to put $1 - \alpha = 1$, the problem involves the solution of a quadratic equation, but when $1 - \alpha$ differs appreciably from 1, Ostwald's Dilution Law no longer applies.

Mass action of a salt.—If to a solution of a *weak* acid a salt of the acid is added the degree of ionisation of the acid will be reduced.

For the ionisation of the monobasic acid we have :



The salt may be regarded as practically completely ionised :



and since the concentration of A' is increased, and

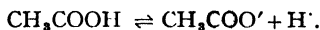
$$[H'] \times [A'] / [HA] = K_a,$$

it follows that $[H']$ must be reduced, *i.e.* the ionisation of the acid is repressed. The effect may be calculated from the law of mass action. In this calculation *the law is applied to the weak acid only* and not to the salt, which is assumed completely dissociated.

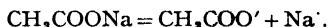
The calculation may also be applied to the effect of adding a strong acid, assumed to be completely ionised, to a solution of a salt of a weak acid MA, also assumed completely ionised. In this case the A' concentration is reduced owing to the formation of the weak acid HA.

EXAMPLE.—To 1 litre of N/10 acetic acid, 1.64 gm. of sodium acetate (mol. wt. 82) are added. Find the hydrogen ion concentration of the resulting solution if K_a for acetic acid at 18° = 1.8×10^{-5} .

The equilibrium for the weak acetic acid is



The sodium acetate is practically completely ionised :



Since the acetic acid is only slightly ionised, and this ionisation is further repressed on adding the sodium acetate, the concentration of the acetate ion is practically equal to that of the sodium acetate :

$$[CH_3COO'] = 1.64/82 = 0.02.$$

The concentration of the acetic acid may be taken as the total concentration of the acid, since very little is ionised :

$$[CH_3COOH] = 0.1.$$

Hence if $[H']$ is the hydrogen ion concentration in the solution of the mixture of acetic acid and sodium acetate :

$$\frac{[H'] \times [CH_3COO']}{[CH_3COOH]} = \frac{[H'] \times 0.02}{0.1} = 1.8 \times 10^{-5},$$

$$\therefore [H'] = 9 \times 10^{-5}.$$

For N/10 acetic acid *alone* we have :

$$(1 - \alpha)V = 1.8 \times 10^{-5}.$$

Since α is very small we can put $1 - \alpha = 1$; also $V = 10$,

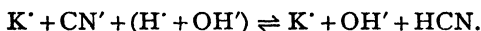
$$\therefore \alpha^2 = 1.8 \times 10^{-6} \text{ approximately,}$$

$$\therefore \alpha = 1.35 \times 10^{-3},$$

$$\therefore [H'] = 0.1 \times 1.35 \times 10^{-3} = 1.35 \times 10^{-4}.$$

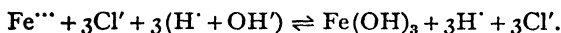
The effect may be shown by adding methyl orange to dilute acetic acid, when a pink colour is produced. On adding sodium acetate the colour changes to yellow.

Hydrolysis.—Salts formed from weak acids or weak bases or both are decomposed by water with production of free acid and base. This reaction is called hydrolysis. The salts themselves are usually largely ionised in solution whilst the weak acid or base is only slightly ionised and its ionisation is further repressed by the common ion of the salt. The hydrolysis is most simply represented as due to the withdrawal of H' or OH' ions from the water by the anion or cation of the salt respectively, so forming the weak acid or base, the other ion of the water remaining free and causing the alkaline or acid reaction. Although only traces of H' and OH' ions are present in water, further ionisation occurs when one ion is withdrawn, since the product of the concentrations is constant: $[H'] \times [OH'] = K_w$. Thus, when the H' ion is withdrawn to form a weak acid, an appreciable concentration of OH' ions results and the solution shows an alkaline reaction, *e.g.* with potassium cyanide :

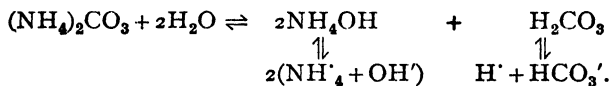


The ionisation of the very weak hydrocyanic acid is almost entirely suppressed by the large excess of cyanide ion from the salt. The solution smells of hydrocyanic acid.

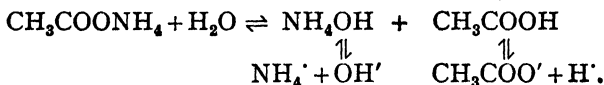
A salt of a strong acid and weak base hydrolyses by withdrawal of OH' ions to form the weak base, and shows an acid reaction; in a solution of ferric chloride, ferric hydroxide is produced in a state of colloidal solution showing a dark-red colour, and the solution has an acid reaction :



A solution of a salt of a weak acid and weak base is hydrolysed, *e.g.* ammonium carbonate :

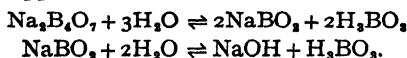


Since in this particular example the base is stronger than the acid the solution reacts alkaline. In the case of ammonium acetate, where the acid and base are equally weak, the reaction is practically neutral :



Hydrolysis is illustrated by the following experiments :

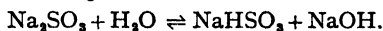
EXPT. 1.—Add phenolphthalein to a cold saturated solution of borax and then acetic acid till the pink colour *just* disappears. Dilute the solution : the pink colour reappears :



The boric acid is so weak that it has no action on the indicator; the caustic soda, a strong base, turns it pink.

EXPT. 2.—Pour 2 to 3 c.c. of 30 per cent. ferric chloride solution into 500 c.c. of boiling distilled water. A deep-red colloidal solution of ferric hydroxide is formed : $\text{FeCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{HCl}$.

EXPT. 3.—Add phenolphthalein to a *concentrated* solution of sodium sulphite and heat. The pink liquid becomes colourless on cooling, but the colour reappears on heating :



The hydrolysis increases when the temperature is raised.

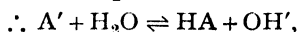
Theory of hydrolysis.—The quantitative theory of hydrolysis may now be explained, a monobasic acid and a monacid base being considered.

(1) Let 1 g. mol. of a salt BA of a *strong* base BOH and a *weak acid* HA be dissolved in V litres of water, and let a fraction x of the salt be hydrolysed ; x is the *degree of hydrolysis*. The salt and strong base are assumed to be completely ionised, and the concentration of OH' ions from the water is neglected in comparison with that from the base :

$$[\text{acid}] = [\text{base}] = x/V$$

$$[\text{unhydrolysed salt}] = (1-x)/V.$$

The reaction is :



and the *hydrolysis constant* is :

$$K_h = [\text{HA}] [\text{OH}'] / [\text{A}'], \dots\dots\dots(1)$$

the water concentration being practically constant. But

$$[\text{OH}'] = [\text{free base}] = x/V; [\text{HA}] = [\text{free acid}] = x/V;$$

$$[\text{A}'] = [\text{unhydrolysed salt}] = (1-x)/V;$$

$$\therefore K_h = (x/V)^2 / [(1-x)/V] = x^2 / (1-x)V. \dots\dots\dots(2)$$

For the ionisation of the weak acid and of water :

$$K_a = [\text{H}'] [\text{A}'] / [\text{HA}], \dots\dots\dots(3)$$

$$K_w = [\text{H}'] [\text{OH}']. \dots\dots\dots(4)$$

Eliminate $[\text{H}']$ by dividing (4) by (3),

$$\therefore [\text{OH}'] [\text{HA}] / [\text{A}'] = K_w / K_a,$$

\therefore from (1),

$$K_h = K_w / K_a. \dots\dots\dots(5)$$

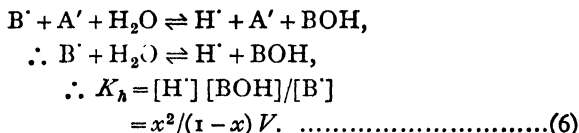
Thus for a salt of a *weak acid* and a *strong base* :

$$\text{the hydrolysis constant} = \frac{\text{ionic product of water}}{\text{dissociation constant of the weak acid}}.$$

(2) In a similar way it is easily shown that for a salt of a *weak base* and a *strong acid*, the hydrolysis constant :

$$K_h = K_w / K_b = \frac{\text{ionic product of water}}{\text{dissociation constant of weak base}}.$$

In this case :



For the ionisation of the weak base and of water :

$$K_b = [B'] [OH'] / [BOH], \quad (7)$$

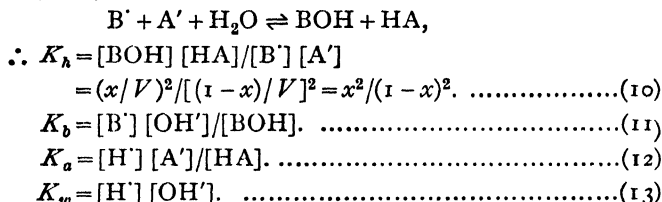
$$K_w = [H'] [OH']. \quad (8)$$

Eliminate $[OH']$ by dividing (8) by (7) :

$$\therefore [H'] [BOH] / [B'] = K_w / K_b,$$

$$\therefore \text{from (6)} \quad K_h = K_w / K_b. \quad (9)$$

(3) For the hydrolysis of a salt of a *weak acid* and a *weak base* :



Multiply (11) by (12) and divide (13) by the product :

$$\therefore K_h = K_w / K_a K_b. \quad (14)$$

It is clear from (10) that the degree of hydrolysis in this case is independent of the dilution.

EXAMPLE.—The dissociation constant for HCN is 1.32×10^{-9} at 18° . The ionic product for water is 1×10^{-14} . Calculate the degree of hydrolysis of an $N/500$ solution of potassium cyanide.

$$\begin{aligned} K_h &= \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.32 \times 10^{-9}} = 7.57 \times 10^{-6}. \\ K_h &= \frac{[HCN][KOH]}{[KCN]} \end{aligned}$$

Let x = degree of hydrolysis.

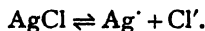
Then $[HCN] = [KOH] = x/500$ and $[KCN] = (1-x)/500$.

$$K_h = 7.57 \times 10^{-6} = \frac{x^2}{(1-x)500},$$

from which $x^2 = 37.85 \times 10^{-4}$ (if $(1-x)$ is nearly 1),

and $x = 6.15 \times 10^{-2}$ or 0.0615.

Solubility product.—Consider a saturated solution of a sparingly soluble salt such as silver chloride in contact with the solid salt. In solution we have the ionisation equilibrium :



If the law of mass action is applied (since the ionic concentrations are very small), we find :

$$\frac{[\text{Ag}^+] \times [\text{Cl}']}{[\text{AgCl}]} = K_s.$$

Since the solution is in equilibrium with the solid, the concentration of the latter will be constant at a given temperature,

$$\therefore [\text{AgCl}] = \text{const.},$$

$$\therefore [\text{Ag}^+] \times [\text{Cl}'] = \text{const.} = K[\text{AgCl}] = K_s.$$

The constant K_s is known as the **solubility product** of the salt.

It may be assumed that the silver chloride concentration $[\text{AgCl}]$ is *approximately* independent of the presence of other substances in the solution. If we add a soluble chloride such as sodium chloride to the solution the value of $[\text{Cl}']$ is increased. With the values of $[\text{Ag}^+]$ and $[\text{Cl}']$ already in the solution, the product $[\text{Ag}^+] \times [\text{Cl}']$ therefore becomes larger than the equilibrium value, and solid AgCl precipitates from the solution until the ionic product $[\text{Ag}^+] \times [\text{Cl}']$ again takes up a value equal to K_s .

If the dissolved silver chloride is assumed to be completely ionised, each molecule will give one silver ion and one chloride ion; hence if the solubility of silver chloride is S mols/litre,

$$S = [\text{Ag}^+] = [\text{Cl}'] = \sqrt{K_s}.$$

Since the law of mass action does not apply accurately to strong electrolytes, *i.e.* those largely ionised, the solubility product equation must be regarded as having only a semi-quantitative meaning in such cases, although for very sparingly soluble salts such as silver chloride it will be approximately valid.

The solubility S of a sparingly soluble salt such as silver chloride may be determined by measurement of the electrical conductivity of a saturated solution (see p. 202).

EXAMPLE.—Solid silver chloride is shaken with 1 litre of a solution of sodium chloride containing 3 grams of the salt. The sodium chloride may be assumed completely ionised. The solubility product of silver chloride at the temperature of the experiment is 9×10^{-11} . Calculate how many grams of silver chloride dissolve. [Mol. wt. of $\text{AgCl} = 143.38$.]

The solubility product is $[\text{Ag}^+] \times [\text{Cl}'] = 9 \times 10^{-11}$.

$$3 \text{ gm. of NaCl} = \frac{3}{58.5} = 5.13 \times 10^{-2} \text{ mols (where } 58.5 = \text{mol. wt. of NaCl).}$$

\therefore concentration of chloride ions from the sodium chloride

$$= [\text{Cl}'] = 5.13 \times 10^{-2} \text{ mols per litre.}$$

Let x mols of silver chloride dissolve in the 1 litre of solution. This produces x mols each of silver and chloride ions, since it may be assumed completely dissociated. Hence

$$[\text{Ag}^+] = x; \text{ total Cl' ion conc. } [\text{Cl}'] = 5.13 \times 10^{-2} + x,$$

$$\therefore x(5.13 \times 10^{-2} + x) = 9 \times 10^{-11}.$$

Since x is seen to be very small x^2 may be neglected, and we have

$$5.13 \times 10^{-3}x = 9 \times 10^{-11},$$

$$\therefore x = 1.75 \times 10^{-8} \text{ mols/lit.},$$

\therefore the number of grams of silver chloride dissolving is

$$1.75 \times 10^{-8} \times 143.38 = 2.5 \times 10^{-7} \text{ gm.}$$

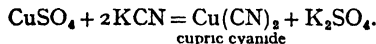
The following experiments illustrate the solubility product principle :

EXPT. 1.—Pass gaseous hydrogen chloride into a filtered saturated solution of common salt, using the apparatus shown in Fig. 96. A white crystalline powder of NaCl falls. This is filtered off in a Buchner funnel (Fig. 1), dried on a porous plate, and heated carefully in a dish to drive off hydrochloric acid ; it is then pure.

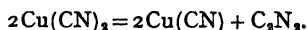
EXPT. 2.—To a saturated solution of silver acetate add : (a) a concentrated solution of silver nitrate, (b) a saturated solution of sodium acetate. In each case silver acetate is precipitated.

Complex ions.—When potassium cyanide (KCN) is added to a solution of a copper salt a complex salt is formed, probably having the formula $K_3Cu(CN)_4$.

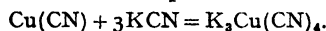
The production of this complex salt is explained in the following equations :



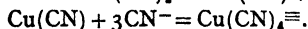
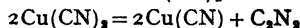
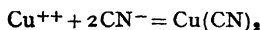
Cupric cyanide is unstable ; it decomposes, cyanogen is evolved, and cuprous cyanide is formed :



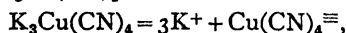
Cuprous cyanide then forms a complex salt with KCN :



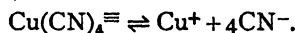
Written in ionic form, these reactions are :



The complex salt $K_3Cu(CN)_4$ is ionised to a considerable extent .



and the cuprocyanide ion gives free cuprous ions and cyanide ions to a slight extent only, thus,

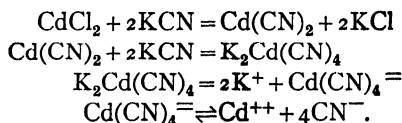


The equilibrium expression for this reaction is

$$K = \frac{[Cu^+][CN^-]^4}{[Cu(CN)_4^{=}]}$$

The equilibrium constant K is known as the **instability constant** of the complex ion $Cu(CN)_4^{=}$, and is usually written $K_{instab.}$

When H_2S is passed into a solution containing the small concentration of cuprous ions produced by the ionisation of the cuprocyanide ions (a concentration diminished by the presence of an excess of potassium cyanide) the solubility product of cuprous sulphide is not exceeded and no Cu_2S is precipitated.* In the case of the complex ion $\text{Cd}(\text{CN})_4^{--}$, produced under similar circumstances from a cadmium salt, the instability constant is larger and the concentration of the cadmium ion $[\text{Cd}^{++}]$ is larger and H_2S produces a precipitate of CdS :



Buffer solutions.—When x c.c. of a given solution of a weak acid such as acetic acid are mixed with y c.c. of a given solution of a salt of the acid such as sodium acetate, a solution is obtained the hydrogen ion concentration of which depends on x and y and is practically unaltered on dilution. The solutions will have a small acidity.

Similarly on mixing solutions of a weak base such as ammonium hydroxide and of one of its salts such as ammonium chloride, solutions with definite alkalinities will be obtained. The alkalinity is measured by the hydroxide ion concentration, $[\text{OH}']$, but since the product $[\text{H}^+] \times [\text{OH}']$ is constant in any aqueous solution (see p. 234), both sets of solutions, acid and alkaline, may be specified by the values of the hydrogen ion concentration, or (as is now more usual) by the pH values (see p. 235).

Such solutions having definite pH values practically unchanged on moderate dilution are called **buffer solutions**. An acid buffer solution should show very little alteration in pH value when small quantities of strong acids are added to it. An alkaline buffer solution should show very little alteration in pH value when small quantities of strong alkalis are added to it.

EXAMPLE.—In $N/10$ acetic acid $[\text{H}^+] = 1.3 \times 10^{-3}$ at 18° . This is calculated from the equilibrium constant

$$\frac{[\text{H}^+] \times [\text{Ac}']}{[\text{HAc}]} = K_a = 1.8 \times 10^{-5}.$$

If now by adding the required quantity of sodium acetate the solution were also made $N/10$ with regard to this salt, the value of $[\text{H}^+]$ will be altered such that we still have $K_a = 1.8 \times 10^{-5}$.

Acetic acid produces only very small concentrations of H^+ and Ac' . Hence the total acetate ion concentration in the solution may be considered to have been produced entirely from the ionisation of the sodium acetate, which may be regarded as completely ionised, $\therefore [\text{Ac}'] = 0.1$.

* See the calculation in Partington and Stratton, *Intermediate Chemical Calculations*, p. 209.

The value of $[\text{HAc}]$ may similarly be considered to be $=0.1$, since the acetic acid (HAc) is weak, and substitution of these values in the above equation gives

$$[\text{H}^+] = \frac{(1.8 \times 10^{-5}) \times 0.1}{0.1} = 1.8 \times 10^{-6}$$

and

$$\text{pH} = 4.74.$$

The above calculation shows that in a buffer solution :

$$[\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]},$$

and this is general for solutions containing a weak acid and its salt. The ratio $[\text{acid}]/[\text{salt}]$ remains practically the same when the solution is diluted and hence so does $[\text{H}^+]$.

It should be noted that $[\text{H}^+] = K_a$ when $[\text{acid}]/[\text{salt}] = 1$ (as in the above example). This provides a means of determining the dissociation constant for a weak acid.

Now let 10 c.c. of N HCl be added to one litre of the solution which is $N/10$ with regard to sodium acetate and acetic acid. The volume change in the solution is disregarded.

The HCl reacts with acetate ions to produce undissociated acetic acid in equivalent amount, so that the normality of the solution with respect to undissociated acetic acid will be

$$\begin{aligned} &0.1 \text{ normal (acetic acid originally present)} \\ &+ 0.01 \text{ normal (acetic acid produced by the added HCl),} \\ &\therefore \text{ total normality of acetic acid} = 0.11. \end{aligned}$$

The $[\text{Ac}^-]$ will be reduced to 0.09 since 0.01 has been removed in the form of un-ionised acetic acid.

On substituting these values in the equilibrium equation we find

$$[\text{H}^+] = \frac{(1.8 \times 10^{-5}) \times 0.11}{0.09} = 2.2 \times 10^{-6},$$

with a corresponding pH value $= 4.66$.

Hence the value of pH has been changed only from 4.74 to 4.66, whilst 10 c.c. of $N\text{HCl}$ added to 1 litre of distilled water would have produced an acidity of pH value $= 2$. Thus the solution considered is a buffer solution in the sense that its acidity is very little altered by adding a small amount of a strong acid. We notice that $[\text{H}^+] = K_a [\text{acid}]/[\text{salt}]$ in this case also.

Mixed solutions of potassium dihydrogen phosphate KH_2PO_4 and disodium hydrogen phosphate Na_2HPO_4 also produce buffer solutions.*

Indicators.—The action of acids and alkalis in changing the colour of indicators is used in testing for these two groups of compounds and in volumetric analysis.

* The calculation for this case is given in Partington and Stratton, *Intermediate Chemical Calculations*, p. 215.

According to Ostwald (1894) indicators are weak acids or bases, one radical of which in the ionic state has a different colour from the undissociated molecule. Thus paranitrophenol is a weak acid, colourless in the undissociated state. A trace of strong acid drives back the slight dissociation and the pale-yellow solution becomes colourless. If a small amount of alkali is added the OH^- ions combine with the H^+ ions of the indicator to form H_2O molecules, and further ionisation of the indicator occurs. The anion of the indicator then shows a strong yellow colour.

Phenolphthalein functions as a very weak acid and its salts, formed by the action of alkalis, are largely dissociated giving an intensely red anion. Its action is similar to that of p-nitrophenol.

Methyl orange is the sodium salt of a sulphonic acid and is largely ionised in solution. The anion is yellow. In presence of acids this anion behaves as a weak base, attaches a hydrogen ion and rearranges to form a red ion which has opposite charges on different parts but is electrically neutral as a whole—a so-called **hybrid ion**. On adding a base, the hydrogen ion is removed and the yellow anion is formed again.

The colour changes of indicators are **due** to changes in structure of the molecules in passing from a "normal" or non-ionised form to an ion or salt form, but these do not affect the **general** theory just stated.

The colour change of an indicator occurs over a certain range of pH, as is seen from Fig. 127. Thus methyl orange changes colour from

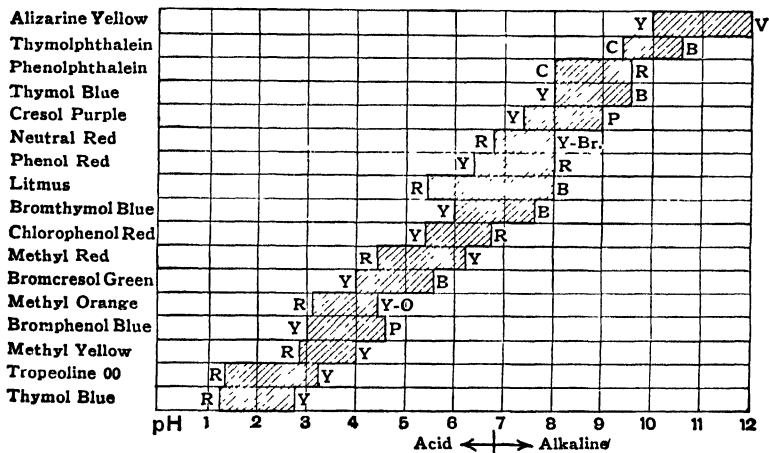


FIG. 127.—Colour change pH intervals of indicators.

Y = yellow. V = violet. B = blue. C = colourless. R = red.
P = purple. Br = brown. O = orange.

red (acid) to yellow (alkaline) as pH changes from about 3 to about 4.5, when the solution is still appreciably acid. Phenolphthalein changes from colourless (acid) to red (alkaline) as pH changes from 8 to 9.5, and its

range is thus in a region of small alkalinity. The function of an indicator may be represented by $X + H^+ = Y$, and the law of mass action gives :

$$[H^+] = K[Y] / [X], \text{ or } pH = pK - \log([Y] / [X]),$$

where K is the indicator constant and $pK = -\log K$. With a two-colour indicator the tint is determined by the ratio $[Y] / [X]$, hence by the pH of the solution and not by the amount of indicator. With a one-colour indicator the depth of colour depends on the indicator concentration and this must be kept the same in comparisons (see Tomiček, "Chemical Indicators", 1951). The following experiments illustrate the theory of indicators.

Prepare a set of buffer solutions as described on p. 248. To 25 ml. of distilled water add 5 or 10 drops of two-colour indicator solution such as methyl red or bromthymol blue. Take 10 ml. of this solution in each of two test-tubes. To one tube add a drop of NaOH solution and to the other a drop of dilute HCl. These tubes give the alkaline and acid colours of the indicator. Now prepare a set of tubes containing 10 ml. of buffer solutions covering the range of the indicator and add to each twice the amount of indicator used in the first two tubes. Hold the acid and alkaline indicator tubes against each other, then on looking through both the tint for $[X] = [Y]$ is seen. The pH of the buffer solution giving the nearest match gives the pK of the indicator.

With the one-colour indicator phenolphthalein, four tubes each containing 10 ml. of suitable buffer solutions and 2 ml. of indicator solution are taken. A fifth tube contains 1 ml. of indicator solution, one drop of NaOH solution, and distilled water to make up 12 ml. The buffer matching this tube gives $pH = pK$.

To determine the pH of a given solution, 10 ml. in a test-tube is mixed with a suitable amount of a two-colour indicator and the tint compared with those of 10 ml. of buffer solutions containing the same amount of indicator. The pH of the matching buffer solution is that of the given solution. As an example, the degree of hydrolysis of a solution of ammonium chloride containing 1.07 gm. of NH_4Cl in conductivity water to 200 ml. may be found. Methyl red is used and the tube containing the NH_4Cl solution is kept corked to exclude air containing carbon dioxide. In this case, since x is small, equations (6) and (9) on p. 240 give :

$$x^2/V = K_h = K_w/K_b, \text{ hence } [H^+] = x/V = \sqrt{(K_w V/K_b)}.$$

The value of K_w may be taken as 10^{-14} and hence x and K_b may be calculated.

The accuracy of pH measurements with indicators is affected by the presence of neutral salts and proteins in solutions and suitable corrections must be made in accurate work.

Titration curves.—The function of an indicator in titrations is to indicate the *equivalence point*, i.e. when equivalent amounts of acid and base are present. In the case of strong acids and bases this will also correspond with the *neutral point* ($pH = 7$), but this is no longer the case

when a weak acid is titrated with a strong base, or a weak base with a strong acid, on account of the hydrolysis of the salts. If the salt has an alkaline reaction (*e.g.* sodium acetate) the indicator range must be in the alkaline region ($\text{pH} > 7$), *e.g.* phenolphthalein, whilst if the salt has an acid reaction (*e.g.* ammonium chloride) the indicator range must be in the acid region ($\text{pH} < 7$), *e.g.* methyl orange or methyl red. With a strong acid and a strong base, any indicator having a colour range between pH values of 3 and 10 can be used.

This point is made clear in Fig. 129, in which the titration curves of 100 ml. of 0.1N hydrochloric and acetic acids by 0.1N NaOH are given. It is seen that for HCl pH undergoes a large change at the equivalence point, so that any one of the range of indicators shown can be used. In the case of acetic acid the change of pH is gradual and the change in passing through the equivalence point is rather small, so that only the indicators phenolphthalein, cresol purple and neutral red are suitable, methyl orange changing colour in the alkaline region.

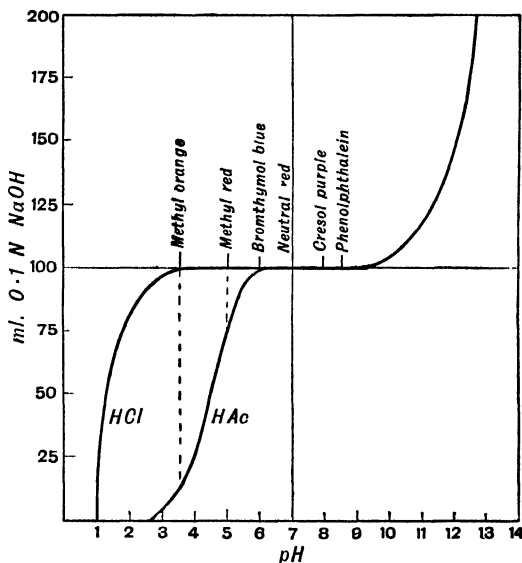


FIG. 129.—Titration curves.

Special indicators. What is called a *universal indicator* shows several colours over a fairly large pH range, *e.g.* from red in acid solution through yellow, green and blue to violet in alkaline solution. They are used in conjunction with buffer solutions, the given solution plus indicator being titrated to the same colour as buffer solution plus indicator. They are not used in ordinary acid-alkali titrations, as the colour change is insufficiently sharp.

If methylene blue is added to methyl orange a *screened indicator* is produced, which is yellowish-green in alkaline solution, passes through grey at $\text{pH} = 4$, and is violet in acid solution. A mixture of bromcresol purple and bromthymol blue is greenish-yellow at $\text{pH} = 6.0$ and blue at $\text{pH} = 6.8$. In this way, the range of each indicator is reduced and the mixture is more sensitive than either separately.

An *oxidation-reduction* ("redox") indicator is one which changes colour in an oxidation-reduction reaction, such as diphenylamine in sulphuric

Meyer in Germany. Odling in 1865 had arranged the elements in a table which shows a close resemblance to Mendeléeff's table of 1869.*

The periodic law.—Mendeléeff's basic idea † was that "there must be some bond of union between mass and the chemical elements; and as the mass of a substance is ultimately expressed in the atom, a functional dependence should exist and be discoverable between the individual properties of



FIG. 130.—D. I. MENDELÉEFF (1834-1907).

the elements and their atomic weights. But nothing, from mushrooms to scientific dependence, can be discovered without looking and trying. So I began to look about and write down the elements with their atomic weights and typical properties, analogous elements, and like atomic weights on separate cards, and this soon convinced me that **the properties of the elements are in periodic dependence upon their atomic weights**; and although I have had my doubts about some obscure points, yet I have never once doubted the universality of this law, because it could not possibly be the result of chance."

* The original tables are reproduced in Partington, *A Short History of Chemistry*, p. 348.

† Mendeléeff, *Principles of Chemistry*, ii, p. 31, 1905.

The original statement of Mendeléeff (1869) includes practically the whole content of the Periodic Law. It is given in eight paragraphs :

(1) The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

(2) Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (platinum, iridium, osmium), or which increase regularly (potassium, rubidium, caesium).

(3) The arrangement of the elements, or of groups of elements, in the order of their atomic weights, corresponds with their so-called *valencies*.

(4) The elements which are the most widely distributed in nature have *small* atomic weights, and . . . sharply defined properties. They are therefore *typical elements*.

(5) The *magnitude* of the atomic weight determines the character of an element [and those of its compounds].

(6) The discovery of many yet *unknown* elements may be expected, for instance elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75.

(7) The atomic weight of an element *may* sometimes be corrected by the aid of a knowledge of those of the adjacent elements.

(8) Certain characteristic properties of the elements can be foretold from their atomic weights.

The periodic table.—Mendeléeff arranged the elements in a table called the periodic table, a modern form of which is given here. In this the elements are arranged in nine vertical columns called *groups*, headed by zero (o) and the Roman numerals from I to VIII, or (as in the table given) the zero group is made a *sub-group* of VIII, each group being subdivided into *a* and *b* as shown. These groups are formed by suitably breaking up into *periods* a continuous series of the elements arranged in the order of their atomic weights. The ordinal numbers called *atomic numbers*, and not the atomic weights, are given in the table. If the periods are written one under the other in horizontal rows, the vertical columns are the groups.

The first period contains two elements, hydrogen and helium ; each of the next two periods contains eight elements. The elements of the third period are analogous to those vertically above them in the second period. In other words, *the properties of successive elements in an earlier period recur in the same order in a later period*. This is seen in the two periods :

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	A

Lithium and sodium, for example, are alkali metals which decompose water in the cold ; fluorine and chlorine are gases which combine very readily with metals and form similar salts, and so on.

THE PERIODIC TABLE
SHORT PERIODIC TABLE

PERIOD.	SERIES.	GROUP.																		
		I.		II.		III.		IV.		V.		VI.		VII.		VIII.			(0)	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	
1	1	H 1																	He 2	
2	2	Li 3		Be 4			B 5		C 6		N 7		O 8		F 9				Ne 10	
3	3	Na 11		Mg 12			Al 13		Si 14		P 15		S 16		Cl 17				Ar 18	
4	4	K 19		Ca 20			Sc 21		Ti 22		V 23		Cr 24		Mn 25		Fe 26	Co 27	Ni 28	
	5		Cu 29		Zn 30				Ga 31		Ge 32		As 33		Se 34		Br 35			Kr 36
5	6	Rb 37		Sr 38			Y 39		Zr 40		Nb 41		Mo 42		Tc 43		Ru 44	Rh 45	Pd 46	
	7		Ag 47		Cd 48				In 49		Sn 50		Sb 51		Te 52		I 53			Xe 54
6	8	Cs 55		Ba 56			Rare Earths 57-71		Hf 72		Ta 73		W 74		Re 75		Os 76	Ir 77	Pt 78	
	9		Au 79		Hg 80				Tl 81		Pb 82		Bi 83		Po 84		At 85			Rn 86
7	10	Fr 87		Ra 88			Ac 89		Th 90		Pa 91		U 92		Transuranium elements 93-					

After argon ten elements instead of eight must be passed over before the periodic recurrence of properties begins again with copper, and a close analogy, *e.g.* that between rubidium and potassium, only after eighteen elements. At the beginning of this period we meet with a difficulty. The element next in order of atomic weight to chlorine is potassium, which undoubtedly belongs to the same group as sodium. The next element is argon, which is an inert gas resembling helium and neon and therefore belongs to the zero, or VIII *b*, group. The order of the atomic weights of potassium and argon is the reverse of the order in the periodic system which brings them into the same groups as their chemical analogues. In such cases, where the atomic weights are apparently inverted, the elements are placed in the groups to which they naturally belong. Three such pairs of common elements are :

1. A 40 K 39 2. Co 59 Ni 58·7 3. Te 127·6 I 126·92
and another case is believed to occur in the last period of radioactive elements, *viz.* thorium (Th) 232 and protactinium (Pa) 230. These supposed anomalies are now easily explained, since the elements concerned are mixtures of isotopes (p. 259).

With this transposition of argon and potassium, the natural sequence runs along the period until manganese is reached. We then expect an inert element resembling argon. Actually we find three elements, iron, cobalt and nickel, with almost identical atomic weights and very similar physical and chemical properties. After these three elements come copper, zinc, etc., which resemble in some respects the elements of Groups I, II, etc., and the inactive element does not appear.

The three elements iron, cobalt and nickel are placed in a separate group, viz. Group VIII *a*, no representatives of which are found in the earlier periods. The elements following, viz. copper, zinc, etc., which do not closely resemble the earlier elements of the same groups, are separated from these by placing them on the right or in *b* positions in the groups, whilst the other elements are placed on the left or in *a* positions.

The elements in Group VIII *a* are called **transitional elements**, and instead of two **short periods** each of eight elements, the whole 18 elements from potassium to krypton inclusive form a **long period**, divided into elements belonging to **even** and **odd series** according as they occur in series of even (*e.g.* K) or odd (*e.g.* Cu) number, beginning with hydrogen.

This first long period is followed after krypton by a second long period beginning with rubidium, followed by the even elements of the period as far as molybdenum. These resemble the corresponding even elements of the preceding long period. After molybdenum comes the element technetium, which is radioactive and is obtained artificially (see p. 267). This is followed by a cluster of three elements with very similar atomic weights and physical and chemical properties, viz. ruthenium, rhodium and palladium. These are obviously **transitional elements** of the same type as iron, cobalt and nickel and **must** therefore be placed in Group VIII *a*. The odd elements of the long period then follow, ending with xenon.

Near the end of this period is a repetition of the inversion of atomic weights met with in argon and potassium. Iodine is a halogen belonging to Group VII, whilst tellurium is an element of Group VI which contains its analogues sulphur and selenium. In the order of atomic weights the positions would be reversed. Again the two elements are placed in those positions which agree with their chemical properties.

A new period begins with cæsium and proceeds as far as lanthanum in Group III in a regular manner. After lanthanum, however, come fourteen elements with atomic weights differing by one, two or even four units, all of which are most closely analogous in chemical properties and very difficult to separate in analysis. These, with lanthanum, and scandium and yttrium in previous periods, are the elements of the **rare earths** (No. 61 is the artificial element promethium). It is obviously impossible to proceed in the normal manner with the rare-earth elements Nos. 57 to 71.

In this case, instead of one element occupying one place in the group there seems to be a cluster of fifteen. These must be placed in the same group as scandium and yttrium, so that the regular change in properties of the elements is checked at this point and goes forward again only when the atomic weight has increased by about 40 units. Then after lutetium, the last rare-earth element, comes the element hafnium discovered in zirconium minerals by Coster and Hevesy in 1923. It is an element of Group IV resembling titanium and zirconium.

After hafnium come tantalum, tungsten, rhenium and then the three transitional elements osmium, iridium and platinum, which fall in

Group VIII *a*. The rest of this long period continues from gold in Group I to bismuth in Group V and the radioactive element polonium in Group VI. Element No. 85 in Group VII is the artificial element astatine and the period closes with the inert radioactive gas, radon, in Group VIII *b* (or Group O). This long period, therefore, contains in all 32 elements.

The numbers of elements in the periods up to this point are 2, 8, 8, 18, 18, and 32. A new period begins with francium in Group I, followed in Group II by radium, and continues as far as uranium, all the elements in this group being strongly radioactive. After uranium come the artificial transuranium elements (p. 268), which are not shown in the table.

Although the short form of the Periodic Table, due to Lothar Meyer, which is given on p. 252, is most convenient for elementary students and for general use, and corresponds with the short table of atomic structures given on p. 263, some teachers prefer the so-called Long Periodic Table, originating with Mendeléeff, a modified form of which is given below, and another form will be found inside the end cover of this book.

LONG PERIODIC TABLE

																H	He																						
																Li	Be	B	C	N	O	F	Ne																
																Na	Mg	Al	Si	P	S	Cl	Ar																
																K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
																Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Os	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Ra								
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No																								

This corresponds with a fuller table of atomic structures. The rectangles enclose elements with incomplete *inner* shells of electrons in the atoms, which are called "transitional elements" in the wider sense, the rare earths (except scandium and yttrium) taking their place inside a

larger period of transitional elements. The double relation of hydrogen to Groups I and VII is also seen.

The periodicity of valency.—Mendeléeff pointed out that the number of a group corresponds with the valency of the elements in it. In some cases (N, S, Cl, Cr, Mn) it is necessary to take the maximum valency, in others (Cu, Ag, Au) the minimum valency, and the assignment of valency seems a little artificial, as Wyruboff (1896) said, but the reason is now fairly clear from the point of view of atomic structure. The valencies are clearly seen with the fluorine and oxygen compounds :

I	II	III	IV	V	VI	VII	VIII
NaF	CaF ₂	BF ₃	SiF ₄	PF ₅	SF ₆	IF ₇	—
Na ₂ O	CaO	B ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Mn ₂ O ₇	OsO ₄

Lothar Meyer's curve.—The periodicity of properties with increase in atomic weight (or atomic number) is strikingly shown (Fig. 131) in the atomic volume curve of Lothar Meyer, in which the atomic volumes (volumes in c.c. occupied by the atomic weight in grams = at. wt. divided by density) are plotted against the atomic numbers, *i.e.* the ordinal numbers of the elements in the periodic table. The atomic volumes rise and fall in a periodic manner. The alkali metals, the atoms of which are unusually bulky, are at the peaks of the curve.

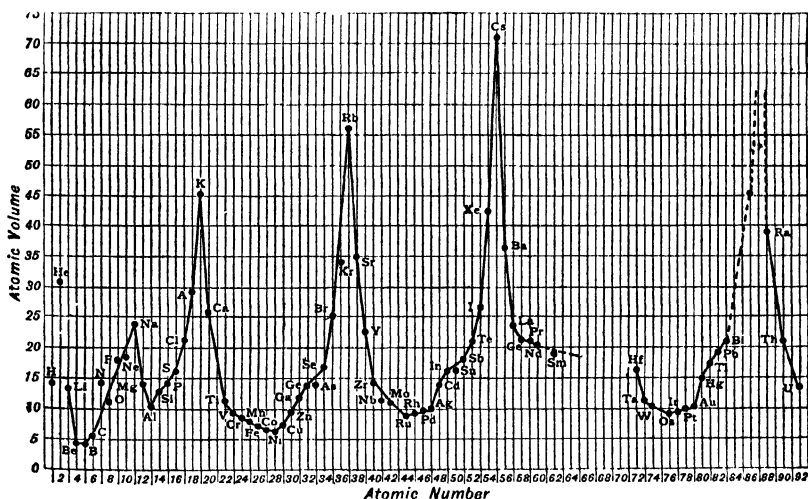


FIG. 131.—Lothar Meyer's atomic volume curve.

Correction of atomic weights.—Mendeléeff, by fixing the positions of the elements in the periodic table, was able to correct some of the atomic weights then in use.

Beryllium was given an atomic weight three times its equivalent ($3 \times 4.5 = 13.5$) since it was thought to be trivalent like aluminium. Its discoverer Avdéeff in 1819 had already pointed out its similarity to bivalent magnesium, and Mendeléeff recognised that its atomic weight is $2 \times 4.5 = 9$, and that it fills a place in Group II otherwise vacant, whilst there is no room in Group III for an element of atomic weight 13.5. Nilson and Pettersson (who had supposed beryllium to be trivalent) found in 1884 that the vapour density of beryllium chloride is 40, which agrees with the formula BeCl_2 (80) but not with BeCl_3 (120). /

Prediction of missing elements.—Mendeléeff in arranging the elements in the periodic system had to leave gaps so that chemical analogies should be preserved. The next element known after calcium ($\text{Ca} = 40$) was titanium ($\text{Ti} = 48$). But titanium if placed after calcium would come in the third group under aluminium, yet its properties show that it is 4-valent and belongs to Group IV under silicon :

Be	9	B	11	C	12	N	14
Mg	24	Al	27	Si	28	P	31
Ca	40	—		Ti	48	V	51
Zn	65	—		—		As	75

There are three vacant places and Mendeléeff predicted that they would be filled by elements still to be discovered, which he called *eka-boron*, *eka-aluminium* and *eka-silicon* (from the Sanskrit, *eka* = one), the properties of which he predicted from their positions in the table. These predictions were brilliantly verified by the discovery of the three elements scandium (Nilson, 1879), gallium (Lecoq de Boisbaudran, 1875) and germanium (Winkler, 1886).

The following table shows the predicted and observed properties in the case of germanium. It was said that these predictions could have been made without the Periodic Law, but no chemist seems to have thought of doing this.

EKA-SILICON (Es) predicted by
Mendeléeff, 1871.

GERMANIUM (Ge) discovered by
Winkler, 1886.

Atomic weight 72.

Atomic weight 72.6.

Density 5.5.

Density 5.47.

Atomic volume 13.

Atomic volume 13.2.

Colour of element: dirty grey,
giving a white powder of EsO_3 ,
on heating in air.

Element is a greyish-white metal,
giving a white powder, GeO_2 , on
heating in air.

Metal will decompose steam with difficulty.

Metal does not decompose water.

Action of acids will be slight : that of alkalis more pronounced.	Metal is not attacked by HCl : it dissolves in <i>aqua regia</i> ; aqueous KOH has no action, but molten KOH oxidises it with incandescence.
Element will be obtained by action of sodium on EsO_2 , or K_2EsF_6 .	Element obtained by reduction of GeO_2 by carbon, or of K_2GeF_6 by sodium.
Oxide EsO_2 will be refractory ; sp. gr. 4.7 ; basic properties less pronounced than those of TiO_2 or SnO_2 , but more marked than those of SiO_2 .	Oxide GeO_2 refractory ; sp. gr. 4.703 ; very feebly basic, although indications of oxy-salts are found.
Hydroxide will be soluble in acids, but the solutions will readily hydrolyse with deposition of meta-hydroxide.	Acids do not pp. hydroxide from dilute alkaline solutions ; from concentrated solutions, acids or CO_2 pp. GeO_2 or meta-hydroxide.
Chloride EsCl_4 will be a liquid, b. pt. below 100° , sp. gr. 1.9 at 0° .	GeCl_4 is a liquid, b. pt. 86.5° , sp. gr. 1.887 at 18° .
Fluoride, EsF_4 , will not be gaseous.	$\text{GeF}_4 \cdot 3\text{H}_2\text{O}$ is a white crystalline solid.
Organo-metallic compounds will be formed ; e.g. $\text{Es}(\text{C}_2\text{H}_5)_4$, b. pt. 160° , sp. gr. 0.96.	$\text{Ge}(\text{C}_2\text{H}_5)_4$, b. pt. 160° , sp. gr. slightly less than that of water.

Results like these convinced chemists that the Periodic Law was of fundamental importance, and about 1890 (twenty years after it was announced) it came into fairly general use in teaching.

Utility of the periodic table.—The periodic table has several advantages over any other system of classification of the elements :

1. It allows the elements to be classified in a very simple way, since only the atomic weights are required in order to place the elements in the table.
2. It includes in itself some previous methods of classification, such as that according to valency.
3. It enables the atomic weight of an element to be checked, since if the wrong multiple of the equivalent had been taken, there would be no place for the element in the table.
4. The existence of an empty space in the table directs attention to an undiscovered element and also, from the position in the table, enables the properties of the elements to be predicted.
5. The periodic table is closely related to much of our new information on the structure of the atom and has proved of great service in this field. It is based on some fundamental law relating to the building up of atoms from their simpler ultimate components, common to all atoms.

THE STRUCTURE OF THE ATOM*

Isotopes.—If the air is pumped out of a glass tube containing an anode and cathode connected with an induction coil it is found that at low pressure a blue glow proceeds from the cathode, producing a green

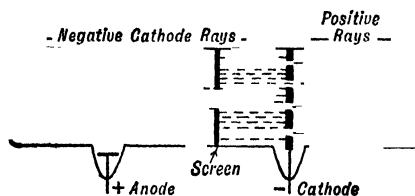


FIG. 132.—

Cathode and positive rays.

fluorescence where it strikes the wall of the tube (Fig. 132). This blue glow, called **cathode rays** (discovered by Plücker in 1859), was shown by Sir J. J. Thomson in 1897 to consist of free negative **electrons**, each with a mass $1/1840$ that of the hydrogen atom, moving with high speeds. They are formed with electrodes of different materials and with different

residual gases in the tube and therefore appear to be a *common constituent of all atoms*.

Goldstein, and Thomson, detected in the cathode ray tube, besides free electrons, **positive rays** (formerly called **canal rays** because they pass *backwards* through small apertures in the metal cathode), but none with a mass smaller than that of a hydrogen atom. Thomson in 1913 also showed that neon consists of a mixture of two kinds of atoms of masses 20 and 22, called **isotopes**. An apparatus devised by Aston is shown in Fig. 133. Modern forms of the apparatus have been much improved and are used in the analysis of gases and also in the accurate determination of atomic weights.

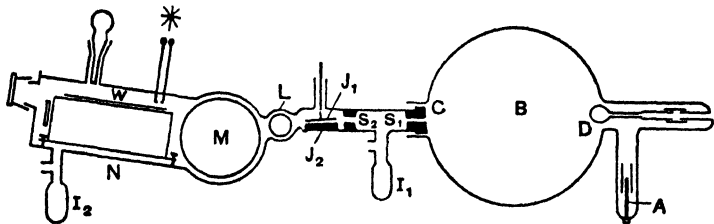


FIG. 133.—Mass spectrograph.

Positive rays produced by an electrical discharge in the gas in the bulb *B* pass through the perforated cathode *C* (the anode is *A*) and then through slits S_1S_2 . The rays then pass through the electric field of a plate condenser J_1J_2 , by which they are deflected downwards, and a fairly narrow pencil goes through a diaphragm (not shown) near the stopcock *L*. The rays then go through a magnetic field at right angles to the electric field and to the plane of the paper at *M* (a section of a magnet pole), so arranged that the downward deflection due to the electric field is compensated. They then reach a focus on the photographic plate *W* in the camera *N*,

producing a line which can be developed. A low pressure is maintained in the part of the apparatus to the left of the bulb by means of pumps and the charcoal bulbs I_1 and I_2 cooled in liquid air. D is a silica bulb which protects the opposite side of the glass bulb B from being melted by the intense beam of cathode rays emitted by C .

The rays corresponding with particles having fixed values of *mass/charge* (m/e) produce a line on the photographic plate resembling a spectrum line, hence the whole apparatus is called a *mass spectrograph*, the set of lines being called a *mass spectrum*. From this spectrum it is possible to calculate the values of m/e for the particles, and hence (if the charges are known) to compare the masses of various particles forming the positive rays. A set of mass spectra is shown in Fig. 134.

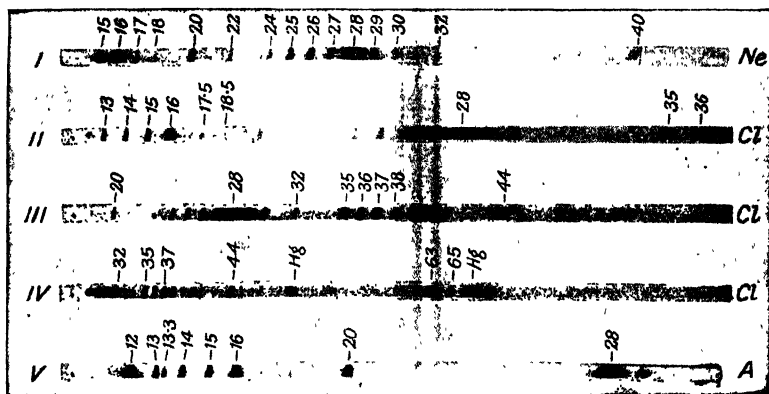


FIG. 134.—Mass spectra.

The lines additional to those of the isotopes of the elements indicated are due to impurities in the discharge tube.

Aston's "Mass-Spectra and Isotopes" (Arnold)

As a result it is found that many common elements are really mixtures of atoms of different masses. Chlorine, for example, gives no line corresponding with the chemical atomic weight 35.5 but two lines corresponding with masses 35 and 37 (together with lines 36 and 38, corresponding with the two hydrogen chlorides). Ordinary chlorine is a mixture of the two varieties or isotopes of chlorine, its mean atomic weight being 35.5. Since no variation in the atomic weight of chlorine has been found, the two varieties must always occur mixed in the same ratio.

Many elements are found to be mixtures of isotopes, *e.g.* carbon of isotopes of masses 12 and 13, nitrogen of isotopes 14 and 15, oxygen of isotopes 16, 17 and 18, potassium of isotopes 39, 40 and 41, etc. The name *isotope* (from the Greek, *isos*, equal, and *topos*, place) denotes that *each place in the periodic table may contain two or more isotopes forming together what was formerly regarded as a single element*. Thus, the place occupied by chlorine includes the two isotopes of chlorine, 35 and 37.

Hydrogen contains isotopes, *viz.* ordinary hydrogen of mass 1 and the

so-called "heavy hydrogen" or deuterium of mass 2, discovered in 1932 by Urey, Brickwedde and Murphy and denoted by the symbol D. Ordinary water contains about 1 part in 6000 of deuterium oxide D_2O , or "heavy water", which can be isolated in the pure state. Deuterium oxide has a density of 1.1, freezes at $+3.8^\circ$ and boils at 101.4° . Although the chemical and physical properties of the isotopes of other elements are so nearly alike that they can scarcely be separated by ordinary means, the properties of hydrogen and deuterium differ sufficiently to allow of separation, say by diffusion.

Atomic numbers.—A discovery of fundamental importance was made in 1913-14 by Moseley, working in Manchester and Oxford. Moseley was unfortunately killed at Gallipoli in the Great War. His work was based on the discovery by Barkla and by Kaye that each solid element when bombarded by cathode rays in a vacuum tube emits X-rays of wave-length characteristic of that element.

These rays may be refracted by crystals, acting like diffraction gratings for ordinary light, and hence may be separated into a spectrum. In this way the wave-lengths of the X-rays can be found. The velocity of light divided by the wave-length gives the frequency. Various types of rays are emitted but one type, the so-called K-rays, appeared to give two lines (really consisting of two pairs of two lines, very close together) as shown in Fig. 135. In this the spectra are placed approximately in register, parts representing the same angle of refraction by the crystal being in the same vertical line.

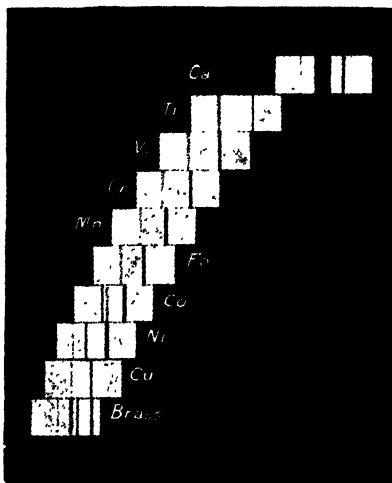


FIG. 135.—X-ray spectra (Moseley)
K-rays.

In 1914 Moseley showed that the square roots of the K-frequencies when plotted against the atomic numbers, *i.e.* the ordinal numbers of the positions of the elements in the periodic table (p. 252), give straight lines. He suggested that *the atomic number is equal to the positive charge on the nucleus of the atom*, the electronic charge being the unit.

Moseley's method provides a method of finding the atomic number from the wave-length of the X-rays, and so enables the place of an element in the periodic table to be fixed. Tellurium and iodine, for example, have atomic numbers of 52 and 53, in the order expected from their chemical properties, whilst their atomic weights place them in the opposite order.

Since most elements are mixtures of isotopes, the atomic weight is only

a mean value and has not much significance. Moseley's method also shows if any elements are missing from the table, since if two elements have atomic numbers differing by unity, no other element can come in between them. It was found that lutetium, the last element of the group of rare earths, had the atomic number 71, whilst the next known element of higher atomic weight, tantalum, had the atomic number 73. An unknown element of atomic number 72 must, therefore, come between lutetium and tantalum. This was sought for and discovered by Coster and Hevesy in 1923; it is the element hafnium. It was found in this way that nearly all the elements within the structure of the periodic table were known.

The structure of the atom.—Dalton and chemists generally throughout the nineteenth century regarded the atom as a kind of minute, hard billiard ball, incapable of division, all the atoms of a given element being exactly alike. The discovery of isotopes disproved the second assumption. Ever since Prout in 1815 had suggested that all elements are formed from the lightest element, hydrogen, chemists also suspected that atoms might be divisible into simpler parts, though what these parts were or how the division was to be made no one knew. With the discovery of radium by Madame Curie in 1898, and the investigation of radioactivity (see p. 265), it became possible to explore the inner structure of the atom.

The atom of hydrogen is pictured by Rutherford as consisting of a very small positively charged **nucleus**, outside which and at a considerable distance from it is a negative electron which neutralises the opposite charge of the nucleus. The nucleus of the hydrogen atom is called the **proton**. An uncharged particle called the **neutron**, of the same mass as the hydrogen nucleus, is also known. The nuclei of atoms heavier than hydrogen are supposed to be built up of protons and neutrons; the number of protons is equal to the positive charge of the nucleus, which is equal to the atomic number; the sum of the protons and neutrons corresponds with the atomic mass. Outside the nucleus are as many electrons as there are protons in the nucleus. Since isotopes have the same atomic number, their nuclei have the same number of protons but different numbers of neutrons. Chlorine, with the atomic number 17, has 17 protons in the nucleus. The isotope of mass 35 has, therefore, 18 neutrons ($17 + 18 = 35$) in its nucleus, while that of mass 37 has 20 neutrons.

The next atom to hydrogen, helium, is supposed to have a nucleus of mass 4 and charge 2, composed of two protons and two neutrons. Outside this nucleus are two electrons. In still heavier atoms the two electrons of the helium atom are retained in an inner shell next to the nucleus, and the remaining electrons are arranged in several shells at increasing distances from the nucleus. The successive atoms in the periodic table may be supposed to be built up as follows.

The positive charge of the nucleus increases by 1 unit for each successive step in atomic number. The mass of the nucleus increases, usually by more than 1 unit, by addition of protons and neutrons. The structures



of the atoms from hydrogen to neon can then be represented as follows :

	<i>Mass of nucleus</i>	<i>Charge on nucleus</i>	<i>Outer electrons</i>
H	1	1	1
He	4	2	2
Li	7	3	2 + 1
Be	9	4	2 + 2
B	11	5	2 + 3
C	12	6	2 + 4
N	14	7	2 + 5
O	16	8	2 + 6
F	19	9	2 + 7
Ne	20	10	2 + 8

When a 2-electron shell is completed with helium, a new shell begins to be formed containing from 1 electron in lithium to 8 electrons in neon. The structures of the next period of atoms higher than neon is a repetition of this, a new shell of 8 electrons being completed with the next inert gas, argon. *The outer shells of all the inert gases contain 8 electrons*, and this stable grouping of an octet of electrons suggests an arrangement at the

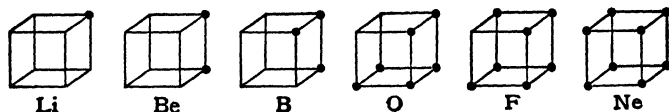


FIG. 136.—Structure of atoms on the octet theory.

corners of a cube (G. N. Lewis, 1916). In Fig. 136 the inner shells are supposed to be inside the cubes, only the outer electrons being shown.

The eight elements in periods 2 and 3 correspond with the completion, step by step, of two successive shells of 8 electrons around the nuclei; the positive charges of the nuclei increase in steps of 1 unit from one element to the next. Periods 4 and 5 contain 18 elements each, so that it is supposed that shells of 18 electrons are completed. Since the outer shells of krypton and xenon each contain 8 electrons, there must be completed shells of 18 electrons below them, the original outer shell of 8 in the case of krypton thus expanding to 18. The electronic structures of the inert gases are therefore :

He	-	-	-	2
Ne	-	-	-	2 + 8
Ar	-	-	-	2 + 8 + 8
Kr	-	-	-	2 + 8 + 18 + 8
Xe	-	-	-	2 + 8 + 18 + 18 + 8
Rn	-	-	-	2 + 8 + 18 + 32 + 18 + 8

Period 6, if we include the element technetium, contains 32 elements, hence 32 electrons are added in succession in passing from xenon to

the radioactive emanation. In passing through the series of rare earths, the *inner* group of 18 electrons of xenon expands to 32, whilst the *outer* group remains as 8+3 (or 9+2) electrons. This explains why the rare earths all belong to the same group and have the same valency.

The arrangement of electrons around the nuclei of the atoms of the elements is shown in the table below. All elements having the same completed groups of electrons (2, 8, 18 or 32) are shown in the same horizontal row, and the vertical columns contain elements with the same number of electrons in the incomplete *outer* groups, shown at the top. The electronic arrangements are read off as follows :

O 2+6

Ca 2+8+8+2

Fe 2+8+14+2

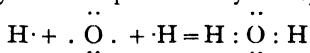
When scandium is reached, instead of the group 2+8+8+3 being formed, the group 2+8+8 expands to 2+8+9 and 2 electrons form an outer shell. In the ion Sc^{+++} these two electrons and one from the inner group are lost, so that the scandium ion has the same outer structure as argon, 2+8+8. The upper limits of co-valencies (see below) 8, 6 and 4 are marked by heavy horizontal lines.

	0	1	2	3	4	5	6	7	2	2	2	2	2	2	2	2	2	1	2	2	2	2
									9	10	11	12	13	14	15	16	18		9	9	9	9
																			19	20	30	31
		H																				
2	He	Li	Be	B	C	N	O	F														
2 8	Ne	Na	Mg	Al	Si	P	S	Cl														
2 8 8	A	K	Ca																			
2 8									Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu					
2 8 18																						
2 8 18 8	Kr	Rb	Sr																			
2 8 18									Yt	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag					
2 8 18 18																						
2 8 18 18 8	Xe	Cs	Ba																			
2 8 18 18									La													
2 8 18																			Ce		Yb	
2 8 18 32									Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au					
2 8 18 32 18																						
2 8 18 32 18 8	Rn	Fr	Ra																			
2 8 18 32 18									Ac	Th	Pa	U										

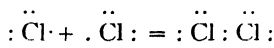
The electronic theory of valency.—A lithium atom reacts with a fluorine atom to form ions Li^+ and F^- by the transfer of the outer electron of the lithium to the shell of 7 electrons of the fluorine. The lithium ion has the electron pair of the helium atom as its outer shell, whilst the fluorine ion has an outer octet of electrons like neon. Owing to the transfer, the

charges of the ions arise. The change is easily visualised from Fig. 136. The chlorine atom has an inner octet (the neon structure) and 7 outer electrons. On reaction with a sodium atom, with an inner completed octet and 1 outer electron, the sodium loses 1 electron and the chlorine gains 1 electron, the ions Na^+ and Cl^- being formed, each with the complete external octet of argon. In such compounds as Li^+F^- and Na^+Cl^- there is *no true valency bond between the ions*, these being held by electrostatic attraction in the lattice (Fig. 56, p. 94), whilst in solution the ions are free. Such a link is sometimes called an **electrovalent link** or an **electrovalency**.

Lewis assumed that *in the formation of an ordinary single valency bond (covalent link or covalency) a pair of electrons is shared in common by two atoms*. In this way one or both atoms (except hydrogen) may complete an octet of electrons. The water molecule is formed from the oxygen atom with 6 electrons and 2 hydrogen atoms each with 1 electron, and the oxygen in water is surrounded by 8 electrons. If the outer electrons are shown by dots the process may be represented by :

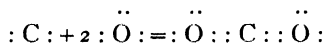


the two valency bonds each containing a shared pair of electrons. The formation of a molecule of chlorine from two atoms of chlorine, each with 7 electrons, may be represented as follows :

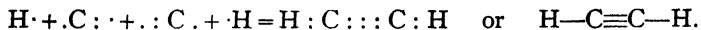


a shared pair of electrons representing the single bond. The chlorine molecule will be $:\ddot{\text{Cl}}:\ddot{\text{Cl}}:$ which is the electronic formula corresponding with the structural formula $\text{Cl}-\text{Cl}$.

A double bond is formed by *four* equally shared electrons, two from each atom. In the formation of carbon dioxide :



the double bonds in $\text{O}=\text{C}=\text{O}$ each have four electrons. A triple bond has three shared pairs of electrons, as in the acetylene molecule :



Wave-mechanical theory of valency—Wave mechanics teaches that the electron does not behave like a point charge as assumed above but as if spread over a space. For the electron in the hydrogen atom this is a sphere (*s* electron). In oxygen two electrons (*p* electrons) behave as if the charge is spread over an hour-glass shape, and in nitrogen three electrons form such “clouds”. A valency bond is formed by the overlapping of *s* and *p* clouds in forming the water (*a*) and ammonia (*b*) molecules shown in Fig. 137.

The electron has some property analogous to a spin about an axis, and only electrons with opposite spins can pair to form valency bonds. If a pair of electrons in an atom have opposite spins they cannot act as valency

electrons, so that the valency depends on the number of electrons with unpaired spins in the outer shell (or two shells) of electrons in the atom.

In the water molecule the two valency bonds are theoretically at right angles, but owing to repulsion between the two hydrogens the angle is greater than 90° , probably 106° . In hydrogen sulphide, H_2S , the valency angle is practically 90° . This type of atom binding is called sp^2s , with one s electron, two p electrons, and one s electron in this order.

Nitrogen has three p electrons and these can occupy singly three p orbits at right-angles, say along the axes of x , y , and z , and hence called p_x , p_y , and p_z orbits (or, usually, *orbitals*). These are shown in Fig. 137*b*. They combine with the s electrons of three hydrogen atoms, as shown, forming the molecule NH_3 . In this the three valency bonds are theoretically at right-angles.

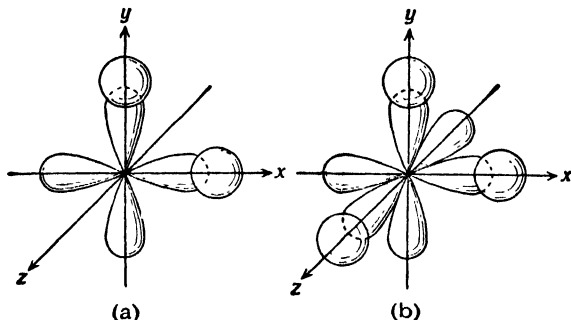


FIG. 137.—Formation of directed bonds.

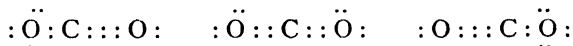
Hybridisation.—The wave-mechanical theory of valency comes into some difficulty in considering the compounds of carbon. The carbon atom has only two p electrons; as is seen from the table on p. 263 it has two s electrons next to the nucleus and four other electrons, of which two are s electrons and two are p electrons, so that the atom is represented by $1s^2 2s^2 2p^2$, the different s atoms, in the first and second shells, being denoted by the figures 1 and 2 before them, and the numbers of electrons by index figures. We might, therefore, expect that a compound CH_2 would be formed with the p electrons, and the s electrons of two hydrogen atoms. It is well known, however, that the compound is CH_4 , methane.

To explain this it is assumed that *one* of the $2s$ electrons gains extra energy, or is "excited", and so becomes a p electron. This gives three p electrons. The remaining $2s$ electron is not now paired with another one (when it is inactive), but is alone and can take part in electron sharing, so that four bonds are formed and, as theory shows, these are arranged tetrahedrally. In the theory of bond formation it is necessary to assume that only electrons with opposite spins can pair to form valency

bonds. In the group $2s^2$, opposite spins are paired, and neither electron has any free spin left, but when the group is split, the separate electrons have their spins unpaired and so can unite with electrons of opposite spins on hydrogen atoms.

There is also another effect involved. When the bond energy exceeds the excitation energy for raising an electron from an s to a p level, the distinction between s and p electrons disappears, and in CH_4 it is incorrect to say that one H is linked by an s electron and three by p electrons. The wave functions are blended or mixed, so that four bonds which are exactly alike are formed. This process is called *hybridisation*, since the resulting wave functions are combinations (or hybrids) of two kinds of functions, the separate characters of which have disappeared in the process.

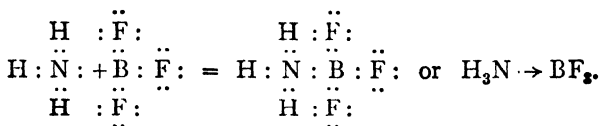
Resonance.—The formula of carbon dioxide on p. 264, namely $:\ddot{\text{O}}::\text{C}::\ddot{\text{O}}:$, indicates that each oxygen is linked to carbon by a double bond consisting of four shared electrons. The wave theory shows, however, that it is possible for electrons to move from one valency group to another. Thus, such a molecule as $:\ddot{\text{O}}:\text{C}:::\text{O}:$ could be formed by a pair of electrons moving on the opposite sides of the carbon nucleus, so that one oxygen is linked by a single bond and the other by a triple bond. It is supposed that this process is taking place, and that the actual state of the carbon dioxide molecule is one having the characters of *three* states as shown below :



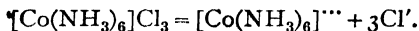
The first and last are not identical, since the motion of the electrons takes place so quickly that the molecule cannot rotate so as to assume the other form in the time available. This is only a figurative way of expressing what happens, but the actual state of the molecule is *one* state having some character of the three states. This phenomenon is called *resonance*, and the molecule is called a *resonance hybrid* of the constituent forms.

Co-ordinate links.—When the pair of electrons required to form a covalent link comes from ~~the same atom~~ instead of being provided by and equally shared between two atoms, a **co-ordinate link** is formed. Co-ordinate links are formed when apparently saturated molecules add on other molecules to form what were previously called “molecular compounds”. Boron has 3 electrons in the outer shell and can share these with 3 fluorine atoms, forming the saturated compound boron trifluoride BF_3 , in which the boron is surrounded by 6 electrons. Nitrogen has 5 outer electrons and shares 3 with three hydrogens forming ammonia NH_3 , with an outer octet around the nitrogen. Of this octet 2 electrons form a *lone pair*, i.e. are unshared. This pair may be *donated* to the boron

atom in BF_3 , so raising the number of electrons round the boron from 6 to 8. The resulting link is denoted by an arrow instead of a line :



For this reason ammonia adds to many metallic salts, forming what are called **co-ordination compounds**, *e.g.* $\text{Co}(\text{NH}_3)_6\text{Cl}_3$. The number of groups co-ordinated with the metal atom (**co-ordination number**) is usually 4 or 6. The atoms or groups attached to the metal (or other "central" atom) in co-ordination compounds are attached by covalencies and are not ionisable; those "outside" the complex nucleus are linked by electrovalencies and are ionisable. Hence the nucleus is often enclosed in square brackets to show that it forms either a neutral molecule or a single ion :



Radioactivity.—In 1896, a year after the discovery of the X-rays by Röntgen, the French physicist Becquerel noticed that compounds of uranium affect a photographic plate wrapped in black paper and he named the effect **radioactivity**. Two years later Schmidt and Madame Curie independently found that thorium compounds produce the same effect. Madame Curie also found that some uranium minerals are four times as active as pure uranium, and the presence in them of some more active substance was confirmed in 1898 by M. and Mme. Curie, who isolated from the uranium ore pitchblende two active bodies, one over a million times more active than uranium, which were called **polonium** (after Mme. Curie's native country) and **radium**.

Investigations of radioactive substances by M. and Mme. Curie, Rutherford and others showed that their properties are due to the emission of three different kinds of **rays**: the α -rays, the β -rays and the γ -rays.

The α -rays are doubly positively charged **helium nuclei** (p. 261) emitted with great velocity, ploughing their way through the atoms of the air, knocking out some of their electrons and so making the air a conductor of electricity and causing the discharge of a gold-leaf electroscope. This property of imparting conductivity to gases is called **ionisation** (see p. 100). Their "range" in air is smaller than that of the β -rays.

When an α -particle collides with a fluorescent screen covered with zinc sulphide, it causes the emission of a flash of light. These flashes may be counted and so the number of α -particles counted, and from this

the number of molecules in 1 c.c. of helium is found. This apparatus is called a *spinharscope*. The α -rays also affect a photographic plate. The positive charge of the α -particles is shown and measured by their deflection in a magnetic field.

The β -rays are free electrons shot off with great velocity, ionising air, affecting a photographic plate, and suffering deflection in a magnetic field in the opposite direction to α -rays (Fig. 139). On account of their small size and great velocity, the β -rays can pass through sheets of metal.

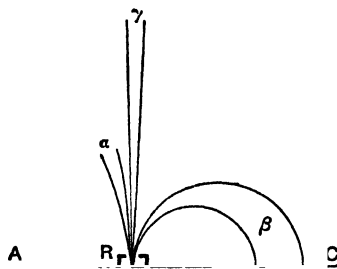


FIG. 139.—Deflection of α - and β -rays from radium by a magnetic field.

The γ -rays are X-rays of very small wave-length. They are not deflected by a magnetic field but ionise air by shaking the electrons out of atoms; they affect a photographic plate and are very penetrating, passing through some inches of lead.

Radium, thorium and a third radioactive element *actinium*, but not uranium, have the property of emitting radioactive gases, formerly called the *radioactive emanations* but now named *radon*, *thoron* and *actinon*. They are isotopes and go into the same place in the periodic table. These gases can be liquefied by dipping the tubes containing them into liquid air, they diffuse like ordinary gases, and refuse to enter into any chemical reactions, so that they belong to the inert gas group (p. 262). They differ from ordinary gases in being radioactive, emitting α -particles, but rapidly lose their activity, radon losing half its initial activity in four days, thoron in less than half a minute, and actinon in a few seconds. The spontaneous production of helium (from the α -particles) from radium emanation was proved by Ramsay.

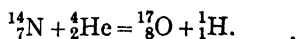
Rutherford and Soddy (1903) explained radioactive changes by assuming that atoms of radioactive elements may spontaneously break up, emitting very swift α - or β -rays carrying large amounts of energy. In the cases of radium, thorium and actinium, the first change is the emission of an α -particle and the production of a gaseous emanation. This emanation in turn emits an α -particle and forms a radioactive solid, which also breaks down in a series of steps. In the case of radium (at. wt. 226) five α -particles are emitted in all and the final inactive product thus has the atomic weight $226 - 5 \times 4 = 206$, which corresponds with an isotope of lead. The final product from thorium has an atomic weight of $232 - 6 \times 4 = 208$, corresponding with another isotope of lead. These isotopes of lead, having different atomic weights, occur in uranium and

thorium minerals. Radium itself is a product of the radioactive decay of uranium.

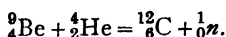
Each radioactive element has a characteristic rate of decay ; the time during which half of a given number of atoms disintegrate is called the *half-life* and varies from a fraction of a second to thousands of years. A disintegration product of thorium, called mesothorium-I, is a by-product in the manufacture of incandescent gas mantles from monazite. It disintegrates rather rapidly, having a half-life of $5\frac{1}{2}$ years as compared with 1700 years for radium, but is cheaper than radium and has been used instead of the latter in making luminous paint for watch dials.

Radium is extracted from the uranium ore pitchblende (U_3O_8) found in Joachimstahl (Czecho-Slovakia), in the Belgian Congo, and on the eastern edge of Great Bear Lake, just south of the Arctic Circle in Canada and the largest fresh-water lake lying wholly within the British Empire. The Great Bear Lake ore is very rich, about 1 gm. of radium in $6\frac{1}{2}$ tons. The radium is recovered by fractional crystallisation of the barium and radium bromides.

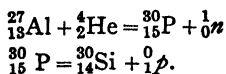
Artificial radioactivity.—When α -rays pass through nitrogen gas, protons (H nuclei) of long range are emitted, which are supposed to come from the nucleus of the heavier element. The nucleus of an atom may be represented by the chemical symbol, the mass by an upper index and the nuclear charge by a lower index ; the above change (Rutherford, 1919) then seems to involve the formation of an isotope of oxygen :



In the bombardment of beryllium with α -particles, neutrons (${}_0^1\text{n}$, mass 1, charge 0) are emitted :

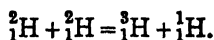


In the bombardment of aluminium with α -particles the change occurs in two stages, since the metal when removed from the rays shows radioactive properties which are due to the emission of positive electrons (${}_1^0\beta$, charge + 1, mass 0). There is first produced an isotope of phosphorus (which can be dissolved and co-precipitated with ordinary phosphoric acid) and the neutron. The phosphorus is radioactive, emits a positive electron, and forms an isotope of silicon :



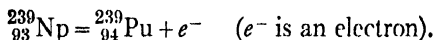
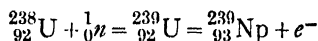
High speed protons, neutrons and deuterons (heavy hydrogen nuclei) also bring about artificial transmutation of atoms which they bombard :

by the collision of deuterium nuclei, a heavier isotope of hydrogen **tritium**, T, of mass 3 is formed :

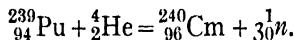
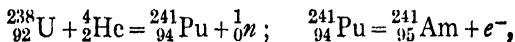


In some cases the bombarding particle enters the nucleus of the struck particle, so that elements are synthesised as well as disintegrated.

When neutrons (p. 261) from a suitable source are slowed by passing through graphite or a deuterium compound (p. 259), they can enter the nucleus of the uranium isotope ${}^{235}_{92}\text{U}$, and the resulting particle undergoes fission into smaller fragments (one of which is an isotope of barium) and the liberation of great amounts of energy: the energy from 1 lb. of uranium is about the equivalent of that formed by burning 10,000 tons of coal. Since neutrons are liberated in the fission, the process may become explosive, and this is the principle of the atomic bomb. The isotope ${}^{235}_{92}\text{U}$ is present only in small quantities in ordinary uranium, which is mostly ${}^{238}_{92}\text{U}$. When ${}^{238}_{92}\text{U}$ is bombarded with neutrons, these enter the nucleus and form ${}^{239}_{92}\text{U}$, which emits an electron to form the artificial element neptunium ${}^{239}_{93}\text{Np}$ (atomic number 93), and this emits another electron to form the artificial element plutonium ${}^{239}_{94}\text{Pu}$ (atomic number 94). In ordinary uranium, some neutrons are produced by the spontaneous fission of ${}^{235}_{92}\text{U}$, which is a neutron producing process. These processes are used in the production of atomic energy :



By bombarding ${}^{238}\text{U}$ and ${}^{239}\text{Pu}$, respectively, with very high-energy helium nuclei, two other radioactive elements of atomic numbers 95 and 96, called americium and curium, are formed :



Elements with atomic numbers higher than 92 are called **transuranium elements**. Besides those mentioned, the elements berkelium (97), californium (98), einsteinium (99), fermium (100), mendelevium (101) and nobelium (102) have been artificially prepared. Some of the transuranium elements may belong to Group III in the periodic table.

CHAPTER XXI

THE ALKALI METALS

THE METALS

Occurrence of metals.—A few metals, *e.g.* gold, platinum, and copper, sometimes occur as such and are then called **native**. In other cases the metals occur as compounds which are called **ores**. These are frequently oxides (*e.g.* of iron and tin), carbonates (*e.g.* of copper and iron), and sulphides (*e.g.* of copper, zinc, lead and mercury). It does not follow that any compound of a metal which occurs abundantly is suitable for the extraction ("smelting" or "winning") of the metal. For example, iron pyrites (FeS_2) is not suitable for the smelting of iron and is not called an "ore" of iron, although some iron is obtained from burnt pyrites left in sulphuric acid works.

The ores of metals are supposed to have been deposited, along with the gangue minerals (see below), from solutions of the materials of the primary rocks. The lower parts of the veins, not exposed to oxidation, contain sulphides, whilst the upper parts, exposed to water containing dissolved air percolating from the surface contain sulphates, carbonates and oxides.

Winning metals from ores.—The method of extraction from an ore varies with the particular metal and the nature of the ore. Generally speaking, oxide ores are directly reduced by carbon to the metal; carbonates are first roasted in air to form the oxides, which are then reduced by carbon; sulphides are first roasted in air to the oxides, sulphur dioxide being evolved, and the oxides may be reduced with carbon, but special methods are sometimes used.

Generally the ore contains rocky impurity, such as silica or silicates, called **gangue**. This is removed as far as possible by mechanical treatment and sometimes **flotation**. The *flotation process* separates minerals such as zinc blende, not easily wetted by water, from galena (an ore of lead) which is. The crushed ore is agitated by a blast of air with water to which a little oil, *e.g.* of eucalyptus, has been added. The blende forms a scum on the surface, whilst the galena sinks.

In some cases mixtures of minerals are separated by making use of the magnetism of one of them. Various forms of magnetic separators are used; in one the crushed ore is carried by a travelling belt passing over a magnetic roller, when it is separated into two parts, the magnetic part being pulled towards the roller (Fig. 140).

To remove the gangue left with the ore, a *flux*, generally quicklime with or without fluorspar, is added during smelting. This combines with the silica to form a fusible mass, *e.g.* of calcium silicate, called *slag*, which floats on the surface of the metal and is easily separated. The slag is generally glassy but opaque when solid. Some slags are used as road material ("road metal") and others as fertilisers (p. 600).

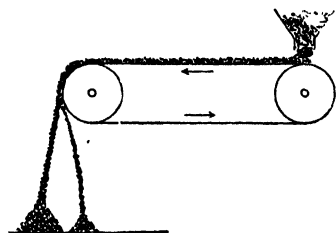


FIG. 140.—Electromagnetic separation (diagrammatic).

Various types of furnace are used in metallurgy (the extraction of metals from ores): in some cases the temperature at which reduction occurs is so high that the electric furnace must be used. A few metals (*e.g.* sodium, aluminium) are obtained by electrolysis, and copper is purified in this way. Generally, however, a furnace fired with coke, coal, or petroleum is used, the combustion being effected either with natural draught, say by a chimney, or by forced blast. The principal methods used for the extraction of metals may be briefly summarised.

Native copper, gold and the platinum metals are worked up by refining. Other industrial processes for the extraction of metals include:

- (1) Reduction of the oxides with hydrogen: tungsten, all metals with atomic weights greater than that of manganese.
- (2) Reduction of oxides with carbon: zinc, cadmium, aluminium (electrolytic), tin, bismuth, manganese, iron, cobalt, nickel, lead, copper; many special steels by simultaneous reduction of the oxide with carbon and iron; metals after Group III, some at high temperature in the electric furnace.
- (3) Reduction of oxides with aluminium (*thermit process*): chromium, manganese (on the small scale magnesium, or *mischmetall*—an alloy of cerium and iron—may replace aluminium).
- (4) Oxidation of sulphides, either directly by atmospheric oxygen as with mercury ($\text{HgS} + \text{O}_2 = \text{Hg} + \text{SO}_2$), or by partial oxidation and interaction of sulphide with oxide or sulphate, as with copper (p. 305) and lead (p. 451).
- (5) Reduction of sulphides with iron: antimony, mercury.
- (6) Electrolytic processes: electrolysis of (a) fused hydroxide for sodium, potassium, etc.; (b) fused chloride for magnesium and calcium, strontium, etc., or the oxide dissolved in fused cryolite for aluminium; (c) solutions of salts for copper, silver, gold, zinc, nickel, chromium; with a mercury cathode for several metals, followed by heating the amalgam.
- (7) Special processes; carbonyl process for nickel (p. 619).

Alloys.—Two or more metals when fused together usually, but not always (*e.g.* zinc and lead, p. 319), form a homogeneous liquid, and the solid formed on cooling is called an **alloy**. The name, used in this sense

by Chaucer, is derived from the Latin, *alligare*, Mediaeval Latin, *alloiare*, "to bind to". Although the preparation of alloys by fusion is the method commonly used, the strong compression of finely powdered metals, the simultaneous electro-deposition of the metals from a mixed solution (*e.g.* copper and zinc in the form of brass, from a solution of the cyanides in potassium cyanide), and the reduction of one or more of the metals from compounds in the presence of the other metal (*e.g.* tungsten and iron compounds in the electric furnace), are alternative processes.

Compounds of metals with non-metals may be present in alloys; hard steel, prepared by quenching, is a solid solution of iron carbide Fe_3C in iron. Alloys of metals with mercury are called **amalgams**, a word which may have been derived from Arabic, *al magma* (Greek, *migma*), a mixture.

The solid formed by the solidification of a fused mixture of metals may be either (a) homogeneous, or (b) heterogeneous. The homogeneous solid alloy may be: (i) *a solid solution*; (ii) *a pure chemical compound*; or (iii) *a solid solution of a compound in excess of one of the metals*. If the solid alloy is heterogeneous, the separate phases may consist of: (i) *pure metals*; (ii) *one or more pure compounds*; or (iii) *solutions of metals or their compounds in metals*.

Metals and non-metals.—The division of elements into metals and non-metals is convenient but rather arbitrary, because there are exceptions to most of the definitions of each. The following table represents the main features of difference, with the important exceptions:

I. PHYSICAL DIFFERENCES

Non-metals :	Metals :
(1) have no lustre (except iodine and graphite).	(1) possess a lustre (except in powder form, although gold, bronze, and aluminium are lustrous even as powders).
(2) are not malleable .	(2) are malleable (<i>i.e.</i> can be hammered into sheets; some metals, <i>e.g.</i> antimony and bismuth, are brittle and crush to powder).
(3) have no tenacity .	(3) have tenacity (<i>i.e.</i> in the form of wire they resist rupture).
(4) have low densities (below 5).	(4) have high densities (several exceptions: lithium has a density of only 0.53; sodium, potassium, magnesium, calcium, and aluminium have low densities).
(5) are poor conductors of heat .	(5) are good conductors of heat (some are not very good).
(6) are poor conductors of electricity (except graphite).	(6) are good conductors of electricity (bismuth and mercury are not very good).

II. CHEMICAL DIFFERENCES

Non-metals :

Metals :

- | | |
|--|---|
| <p>(1) form acidic oxides (<i>e.g.</i> SO_3, P_2O_5); some oxides (<i>e.g.</i> H_2O, CO, N_2O) are neutral.</p> <p>(2) form halogen compounds completely decomposed by water which are not true salts (<i>e.g.</i> PCl_5; CCl_4 is not decomposed by water).</p> <p>(3) are electronegative elements (see p. 192), <i>i.e.</i> form anions, or else show hardly any electrochemical properties (<i>e.g.</i> carbon).</p> <p>(4) usually do not form complex salts (boron and silicon form complex fluorides, KBF_4, K_2SiF_6).</p> | <p>(1) normally form basic oxides (<i>e.g.</i> Na_2O, CuO, Fe_2O_3), but some (ZnO, Al_2O_3) may also act as feebly acidic oxides in presence of strong bases, and some metallic oxides of higher valency (CrO_3, Mn_2O_7) are acidic.</p> <p>(2) form halogen compounds stable in presence of water (KCl, PbCl_2) or decomposed only to a limited extent, the decomposition being reversible:
 $\text{BiCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{HCl}$.</p> <p>(3) are electropositive elements, <i>i.e.</i> form cations; metals may sometimes form part of complex anions, <i>e.g.</i>
 $\text{KAg}(\text{CN})_2 \rightleftharpoons \text{K}^+ + \text{Ag}(\text{CN})_2^-$.</p> <p>(4) form complex salts in which the metal is sometimes in the cation, <i>e.g.</i> $[\text{Co}(\text{NH}_3)_6]^{+++}$, and sometimes in the anion, <i>e.g.</i> $\text{Fe}(\text{CN})_6^{----}$.</p> |
|--|---|

The spectroscope.—When the light from a platinum wire heated by an electric current is passed through a glass prism, at lower temperatures the red end of the spectrum alone appears, corresponding with the red light emitted by the wire. With increasing temperature the visible spectrum extends gradually towards the violet, and a dazzling white light forms a continuous spectrum.

Small quantities of various salts, such as chlorides, heated on platinum wires in a non-luminous bunsen flame, impart characteristic colours to the flame :

sodium salts : yellow
 potassium salts : lilac
 lithium salts : crimson

thallium salts : green
 strontium chloride : red
 calcium chloride : orange-red.

When the light emitted by each of these coloured flames is passed through a prism, the spectra are not continuous but consist of separate lines, each corresponding with a definite wave-length (**line spectra**); incandescent gases and vapours produced by the volatilisation of salts in

the flame differ from solids or liquids in emitting line spectra instead of continuous spectra, and the spectrum of every element is characteristic and serves for its identification. This is the principle of **spectrum analysis**, introduced into chemistry by Bunsen and Kirchhoff in 1859.

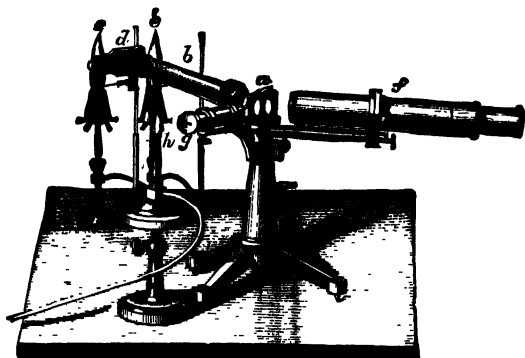


FIG. 141.—Simple spectroscope.

The spectroscope invented by Bunsen and Kirchhoff is shown in Fig. 141. It consists of a prism *a* of flint glass, supported on an iron stand, and a brass tube *b* called a collimator, which is fitted at the end furthest from the prism with an adjustable slit *d*. In this way a narrow line of light from the bunsen flame *e*, in which the substance is heated, is focused on the prism, the rays being made parallel by a lens in the collimator. The light passing through the prism is received by the telescope *f*, which may be moved round so as to embrace any part of the spectrum, and contains a lens which gives a magnified view of the spectrum in the eyepiece. In order to fix the position of any particular line, the image of a glass scale fixed in the third tube *g*, and illuminated by a luminous flame, is thrown by reflection from the face of the prism into the telescope, and appears above the spectrum. The position of the line is read off by comparison with this scale.

The line spectra of salts usually correspond with those of the metals contained in them ; that of sodium chloride, for example, is identical with the spectrum of metallic sodium. The salt vapours at the high temperature of the flame are dissociated into their elements. In some cases a compound exhibits a **band spectrum** superposed on that of the metal. This is the case with calcium chloride, which first gives a spectrum of the chloride, and later a spectrum corresponding with calcium oxide. Band spectra are generally produced by molecules, line spectra by atoms (Fig. 142).

A spectroscope of high resolving power, which separates the different lines as widely as possible, shows that the bands consist of large numbers

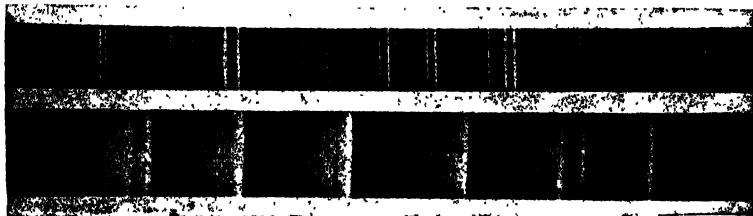


FIG. 142.—Line and band spectra of nitrogen.
(By courtesy of Prof. A. Fowler.)

of fine lines which crowd together at the sharp edge ("head") of the band.

The elements rubidium, caesium, gallium, indium, thallium and helium were discovered by spectrum analysis, which is usually a very sensitive analytical method: a three-millionth of a milligram of sodium is detectable.

THE ALKALI METALS

Group I of the Periodic Table contains two groups of metals: (1) the *even series* or sub-group *a*, consisting of the alkali metals lithium, sodium, potassium, rubidium and caesium (the element of atomic number 87 is the radioactive francium), and (2) the *odd series* or sub-group *b*, comprising copper, silver and gold. Hydrogen is sometimes added to the even series, as it resembles the alkali metals in many respects.

The odd and even series in this group differ markedly, and it was not until Mendeléeff put forward the Periodic Law that chemists would have thought of classing the alkali metals in the same group with copper, silver and gold, which used to be put into different groups, copper with lead and silver and gold with mercury and platinum. The sole resemblance between the odd and even series in Group I is that the members of both can form compounds MX , in which the metals are univalent; metals of other groups, however, can also form such compounds, *e.g.* indium and thallium. Copper, silver and gold, which show varying valencies, in many ways resemble transitional elements (p. 254) and are now often regarded as such.

Even series or sub-group *a*

The alkali metals are strongly electropositive elements, forming basic oxides Na_2O and K_2O . They also form peroxides Na_2O_2 and KO_2 on combustion in oxygen (p. 114). The metals are univalent, *e.g.* they form salts of the type MX with a halogen X . Some compounds with more than one atom of halogen, *e.g.* RbI_3 , CsI_3 , $KI_3 \cdot H_2O$, etc., are known, but in these it is probably the halogen which shows a higher valency.

The alkali metals are reduced from their compounds only with diffi-

culty; the hydroxides are reduced by carbon at high temperatures but most easily by electrolysis. The metals usually show electrovalency (p. 264), although some covalent compounds are known, *e.g.* with alkyl radicals, such as lithium ethyl $\text{Li}(\text{C}_2\text{H}_5)$. In accordance with their strongly electropositive character the alkali metals are the only metals forming stable solid bicarbonates. They all combine directly with hydrogen, forming solid salt-like hydrides MH , decomposed by water: $\text{MH} + \text{H}_2\text{O} = \text{MOH} + \text{H}_2$. These are electrolytes when fused, hydrogen being liberated at the anode; hence they contain the negative hydrogen ion, M^+H^- . The alkali metals combine with halogens, oxygen and sulphur, but (except lithium) not directly with nitrogen. The vapour densities of sodium and potassium correspond with monatomic molecules.

Since the ammonium compounds, containing the positive univalent ammonium ion NH_4^+ , show very close resemblances to compounds of the alkali metals they are usually studied along with the latter.

SODIUM

History.—Metallic sodium was discovered by Davy* in 1807; the method (electrolysis of fused caustic soda) was first tried with potash and potassium was the first alkali metal to be isolated. Davy says:

"A small piece of pure potash which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface [by attraction of moisture, and slight deliquescence], was placed upon an insulated disc of platina, connected with the negative side of the battery . . . in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. . . . The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered with a white film which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash."

The experiment may be carried out by laying a piece of moist stick potash on a piece of platinum foil connected with the negative pole of a battery, and touching the potash with a platinum wire connected with the positive pole.

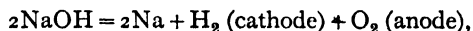
Gay-Lussac and Thenard in 1808 showed that when molten caustic potash or soda is brought in contact with red-hot iron turnings, the iron is oxidised and the alkali metal distils off. At the same time a considerable

* See *Alembic Club Reprint* No. 6.

amount of hydrogen is evolved. The caustic alkalis were then recognised as **hydroxides**, KOH and NaOH, of the metals potassium and sodium, not the oxides as Davy supposed.

The presence of hydrogen in caustic potash or soda may be shown by heating a mixture of the powdered alkali with iron filings in a hard glass tube. Hydrogen is evolved, and may be ignited at a jet fixed to the tube.

Metallic sodium.—Sodium may be obtained by heating sodium peroxide with carbon, or sodium hydroxide with magnesium. Although first prepared by Davy from sodium hydroxide by electrolysis :



metallic sodium was produced on the large scale by a process due to Castner (1886) : sodium hydroxide was heated with carbon and iron at 1000° : $6\text{NaOH} + 2\text{C} = 2\text{Na} + 3\text{H}_2 + 2\text{Na}_2\text{CO}_3$. In 1890 Castner, on account of the development of cheap electricity, was able to revert to Davy's original process and sodium is now produced by this method.

The sodium hydroxide is fused in a cylindrical iron pot (Fig. 143) by gas-burners. A cylindrical iron cathode passes up through the base and is sealed by solidified sodium hydroxide into a prolongation of the pot. The

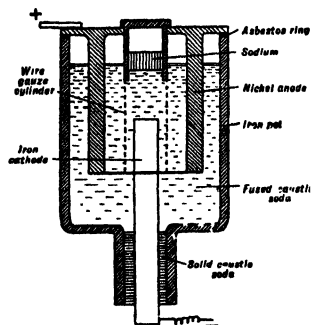


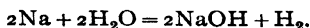
FIG. 143.—Production of sodium by electrolysis.

anode is a cylinder of nickel in electrical connection with a wire-gauze cylinder surrounding the cathode. The metal rises from the cathode and floats on the surface of the sodium hydroxide inside a small metal receptacle provided with a lid. It is removed by a wire-gauze spoon, which allows the fused sodium hydroxide to flow away but retains the sodium. The latter is sent out sealed up in tin cans in the form of thick rods.

In the United States sodium is made by the electrolysis of fused sodium chloride in the *Downs cell* which is similar to the Castner cell except that the central electrode is an anode of carbon from which chlorine is evolved ; it is surrounded by an annular iron cathode on which the sodium deposits.

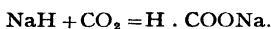
Sodium is a silver-white, very soft metal of low melting point. It may be obtained in octahedral crystals on slow cooling of fused sodium. It is lighter than water. It is a good conductor of electricity. Sodium forms a purple vapour. The clean, freshly-cut surface of the metal rapidly tarnishes in the air, so that the metal is usually kept under petroleum.

It burns when heated in moist oxygen or chlorine, and acts violently on water :



When a small piece of sodium is thrown on water it moves about rapidly, hydrogen being evolved. The rise in temperature is not sufficient to kindle the hydrogen unless the piece of metal is kept in one place by putting it on starch jelly, when the hydrogen burns with a flame coloured yellow by sodium vapour. (Explosions sometimes result.) *Sodium amalgam* is obtained by pressing small pieces of the metal into mercury in a mortar by means of a pestle ; each piece reacts with a small explosion and a flash of light. The amalgam is solid if more than 1 part of sodium is added to 80 of mercury.

Sodium hydride.—Sodium hydride Na^+H^- is prepared by passing a slow stream of dry hydrogen over sodium in a nickel boat heated in a glass tube. Colourless matted crystals form on the upper cooler portion of the tube just beyond the boat. It is decomposed by water with evolution of hydrogen: $\text{NaH} + \text{H}_2\text{O} = \text{NaOH} + \text{H}_2$, and by concentrated sulphuric acid with formation of sulphur and hydrogen sulphide. On heating it dissociates: $2\text{NaH} \rightleftharpoons 2\text{Na} + \text{H}_2$. It absorbs carbon dioxide, producing sodium formate:



Sodium chloride.—Sodium chloride NaCl , common salt, occurs in nature in cubic crystals of *rock salt*, colourless when pure but often tinged yellow, brown, or sometimes blue, by impurities. Rock salt also occurs in large masses which readily break into small cubes. The richest English deposits are in Cheshire ; salt is also found in most other parts of the world. More or less concentrated (about 25 per cent.) solutions (*brines*) also occur in many places, or are artificially produced by letting water down to the rock salt and then pumping. The waters of the Dead Sea and the Great Salt Lake of Utah are concentrated solutions of common salt. The Dead Sea water is also rich in bromides, and is now an important source of bromine : it is evaporated, when much common salt separates out, and the residual liquor is then worked for bromine by chlorination (p. 178). Some salt is made in hot climates from sea water (2.5-3 per cent. NaCl), which is allowed to evaporate in large flat ponds called "salt meadows" by the heat of the sun, such salt being called "solar salt". The mother liquor is called *bittern* and contains magnesium bromide.

Usually the brine is evaporated in large flat iron pans over fire flues. The more slowly the evaporation proceeds the larger are the crystals of salt formed : the grades are fine (or table) salt, manufacturer's salt,

fishery salt, and bay salt (usually in the form of floating "hoppers", or cubes with hollow faces). In modern works the brine is evaporated in multiple-effect vacuum pans with steam heat, the calcium and magnesium salts having first been separated by adding lime and then sodium carbonate.

Pure sodium chloride is made in the laboratory by precipitating a saturated solution of common salt with hydrogen chloride gas (p. 242). It forms a saturated solution in water at 15° containing 35·8 parts of salt to 100 of water (26 per cent.) and the solubility increases only very slowly with rise in temperature. By cooling a saturated solution to -10°, or by cooling a hot saturated solution in hydrochloric acid, a hydrate $\text{NaCl} \cdot 2\text{H}_2\text{O}$, is deposited.

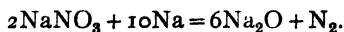
Common salt is used in flavouring and preserving food, preserving hides, as an industrial source of soda, hydrochloric acid and chlorine, in "salting out" soap, melting snow on roads, and glazing common stoneware.

In "salt glazing" stoneware (*e.g.* drain-pipes) common salt is thrown into the furnace in which the goods are fired and is volatilised. In presence of water vapour and the silica of the clay, the salt forms a fusible silicate glaze and hydrochloric acid is evolved:



Sodium bromide NaBr and **sodium iodide** NaI , are similar to the chloride in general properties and are prepared as explained on pp. 181 and 188, respectively. From hot solutions they form anhydrous cubic crystals, but by evaporating at room temperature, monoclinic crystals containing $2\text{H}_2\text{O}$, isomorphous with the corresponding sodium chloride hydrate, are deposited. **Sodium fluoride** NaF is made by neutralising hydrofluoric acid with sodium hydroxide, and forms anhydrous cubic crystals rather sparingly soluble in water. **Sodium hydrogen fluoride** NaHF_2 or $\text{NaF} \cdot \text{HF}$ is prepared by the reaction $\text{NaF} + \text{HF} = \text{NaHF}_2$.

Sodium oxides.—The two common oxides of sodium are the **monoxide** Na_2O , and the **dioxide** (or **peroxide**) Na_2O_2 . Sodium monoxide is obtained either by burning sodium at 180° in a limited supply of air or oxygen and distilling off the excess of metal in a vacuum, or by heating sodium peroxide, nitrate, or nitrite with sodium:



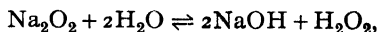
It is a white amorphous mass which decomposes at 400° into the peroxide and metal. It reacts violently with water:



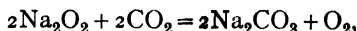
but does not absorb carbon dioxide at the ordinary temperature.

Sodium peroxide is easily obtained by burning sodium in excess of air or oxygen. It is manufactured by heating sodium in aluminium trays

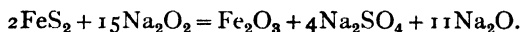
in a current of purified air in iron pipes. In another process the sodium is burnt to monoxide in a revolving iron drum and the monoxide then transferred to a second heat-lagged revolving iron drum where it is oxidised by air to the peroxide. Sodium peroxide is yellow, becoming white on exposure to air from formation of sodium hydroxide and carbonate. When very strongly heated it evolves oxygen. A solution may be prepared by adding the powder in small quantities at a time to a well-stirred mixture of ice and water, a crystalline hydrate $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ being formed. The liquid is strongly alkaline, owing to hydrolysis :



and on warming oxygen is evolved from the hydrogen peroxide. Carbon dioxide decomposes sodium peroxide with evolution of oxygen :



hence the solid has been used for purifying air in confined spaces (*e.g.* in submarines). Carbon monoxide is absorbed : $\text{Na}_2\text{O}_2 + \text{CO} = \text{Na}_2\text{CO}_3$. The solution is an oxidising agent, *e.g.* it converts chromic hydroxide into sodium chromate ; and the fused oxide shows powerful oxidising properties, converting chrome-ironstone FeCr_2O_4 into ferric oxide and soluble sodium chromate (p. 557). It also oxidises iron pyrites :



If a little sodium peroxide mixed with sawdust is placed on filter paper and moistened with water, the mass inflames. Glacial acetic acid inflames when the peroxide is dropped into it. If sodium peroxide is mixed with pieces of recently ignited charcoal and heated in a covered porcelain crucible, a violent reaction occurs and metallic sodium condenses on the lid of the crucible : $3\text{Na}_2\text{O}_2 + 2\text{C} = 2\text{Na}_2\text{CO}_3 + 2\text{Na}$.

Sodium peroxide is used for making "perborate" (p. 370) and also benzoyl peroxide for bleaching flour.

Sodium hydroxide.—Sodium hydroxide or *caustic soda* is obtained very pure by dropping small bits of sodium, or sodium wire from a sodium press, into previously boiled and cooled distilled water in a silver dish, evaporating the solution and fusing the sodium hydroxide (m.p. 318°). Caustic soda is made on the large scale :

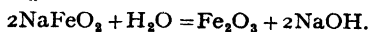
(1) By the electrolysis of a solution of common salt. In the Solvay cell (p. 153) very pure sodium hydroxide is obtained by way of sodium amalgam ; in cells in which the brine is not mechanically separated from the sodium hydroxide produced, the solution also contains undecomposed common salt, say 12 per cent. of each. It is then evaporated in a vacuum evaporator with an arrangement for removing the common salt which separates. When it contains 50 per cent. of NaOH, only 1 per

cent. of NaCl remains. The solution is then evaporated in iron pots over a free fire and the sodium hydroxide finally fused.

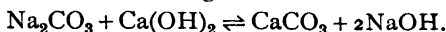
(2) In the **Löwig process**, a mixture of soda-ash and ferric oxide is heated to bright redness in a revolving furnace, when **sodium ferrite** NaFeO_2 is formed:



The mass is cooled, broken up, and thrown into hot water, when the ferrite hydrolyses with formation of sodium hydroxide and insoluble ferric oxide, which is used again:



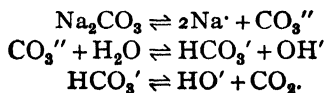
(3) By heating a 20 per cent. solution of sodium carbonate with slaked lime in an iron vessel fitted with agitators:



The reaction is reversible, but by using an excess of lime and a solution of sodium carbonate which is not too concentrated, fairly pure sodium hydroxide solution is obtained. The filtered solution is evaporated as before, and the sodium hydroxide fused. The commercial caustic soda is supplied fused in drums, or in the form of sticks, coarse powder, or pellets; the last is a convenient form for laboratory use.

Sodium hydroxide is a white slightly translucent solid with a fibrous crystalline texture. It is a powerful caustic, breaking down the proteins of the skin and flesh to a pasty mass. When exposed to the air it first deliquesces from absorption of moisture and a little carbon dioxide, forming a saturated solution. The solution then slowly resolidifies from absorption of carbon dioxide, when the carbonate Na_2CO_3 , which is sparingly soluble in sodium hydroxide solution, is formed. Potassium hydroxide does not resolidify, since potassium carbonate is readily soluble, and for this reason a concentrated solution of potassium hydroxide is used in gas analysis to absorb carbon dioxide, since it does not deposit solid which would choke the apparatus. There are several hydrates of sodium hydroxide, *e.g.* $\text{NaOH} \cdot \text{H}_2\text{O}$, $\text{NaOH} \cdot 2\text{H}_2\text{O}$.

Sodium carbonate.—Anhydrous sodium carbonate (*soda-ash*) is a white amorphous powder which aggregates on exposure to moist air owing to the formation of hydrates. When added to water much heat is evolved, and the hydrated salt formed usually sets to a mass, which then slowly dissolves. The solution is distinctly alkaline owing to hydrolysis (the decinormal solution is about 3 per cent. hydrolysed) and on boiling it slowly loses carbon dioxide:



On evaporating the solution and cooling, large monoclinic crystals of *washing soda* $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ are deposited. These effloresce in air and on gentle heating, forming a white powder of the monohydrate $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, also deposited from hot solutions and known as *crystal carbonate*. Other hydrates are known.

Solutions containing less than 6.3 g. Na_2CO_3 per 100 g. water deposit ice on cooling (curve *AB*, Fig. 144). *B* is the eutectic point at -2.1° , where ice, solid $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ and a solution containing 6.3 g. Na_2CO_3 per 100 g. water are in equilibrium with water vapour. More concentrated solutions do not exist in *stable* equilibrium with ice and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, yet a solution of 18.46 g. Na_2CO_3 in 100 g. water may on cooling become unsaturated with respect to decahydrate and deposits ice at -7.5° . *BC* is the stable part of the solubility curve of decahydrate (the ordinary "solubility curve"). At *C* the solid decahydrate changes at 32° into a rhombic heptahydrate, $\alpha\text{-Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$. *CD* is the stable solubility curve of this salt, which may be prolonged on both sides into metastable regions shown by dotted lines. At *D* the heptahydrate changes at 35.4° into monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, the solubility curve of which, with a prolongation into a metastable region shown dotted, is *DE*. Another heptahydrate, $\beta\text{-Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, which is always metastable, separates along *FG*.

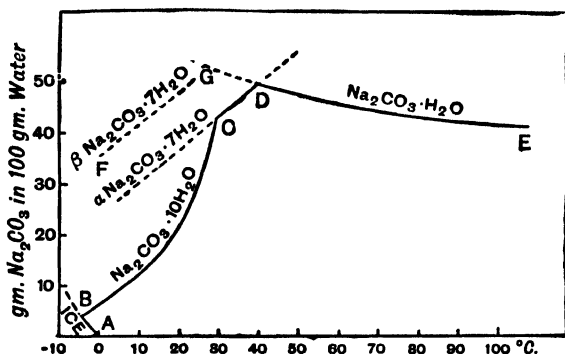
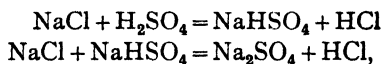


Fig. 144.—Solubility curves of sodium carbonate.

A compound of sodium carbonate with sodium bicarbonate is **sodium sesquicarbonate** $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, which occurs native as *trona* or *uraolite* in various localities and is produced by the spontaneous evaporation of soda lakes, e.g. in Egypt. Large deposits occur in Owens Lake in California, and Lake Magadi in British East Africa. The sesquicarbonate is also made artificially by crystallising equimolecular amounts of carbonate and bicarbonate from a solution in warm water; the artificial salt is known as *concentrated soda crystals* and is used in wool washing. It is neither efflorescent nor deliquescent.

Sodium carbonate is manufactured from common salt by two processes, viz. the Leblanc process (which is now almost obsolete) and in large amounts by the Ammonia-Soda process.

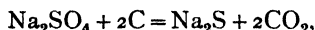
The Leblanc process.—In this process, invented by Nicholas Leblanc (Le Blanc) in 1787, sulphuric acid is heated with common salt to form sodium sulphate (*salt-cake*) as described on p. 156 :



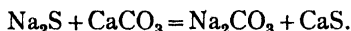
the hydrochloric acid being absorbed in water.

The sulphuric acid may be made from pyrites, in which case the burnt pyrites may contain copper and sometimes silver and gold, which are extracted as a part of the process.

The salt-cake is then mixed with carbon (coal slack) and crushed limestone and heated in a *black-ash furnace*, which is a large revolving iron cylinder lined with firebricks, through which flames from a gas producer pass. The sodium sulphate is reduced to sulphide by the carbon :



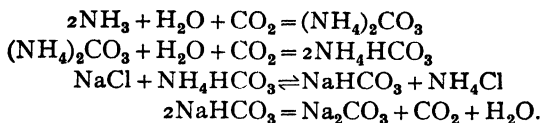
and the sulphide then reacts with the limestone to form sodium carbonate and calcium sulphide :



When the reaction is complete the pasty mass is discharged through a man-hole and when cool is lixiviated with water in tanks to dissolve the sodium carbonate, leaving the calcium sulphide as *alkali waste*, from which the sulphur is recovered (p. 542). The solution may be evaporated in pans to produce crude sodium carbonate, but is now usually heated with slaked lime to form caustic soda (p. 280).

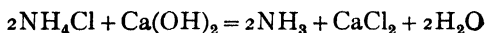
The complete Leblanc process is obsolete, but large quantities of salt-cake are made for use in the sulphate process for making cellulose from wood pulp.

The ammonia-soda process.—When carbon dioxide is passed into a nearly saturated solution of common salt containing ammonia, ammonium carbonate is formed and this then tends to pass into ammonium bicarbonate, which enters into reaction with the sodium chloride to form sodium bicarbonate and ammonium chloride. Since sodium bicarbonate is sparingly soluble in a solution of sodium chloride or ammonium chloride, it mostly separates out as a solid which may be filtered off and heated to form sodium carbonate :

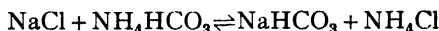


The reaction was discovered by Fresnel about 1810. It was worked for a year or two in Scotland by John Thom in 1836 but was not successful. Dyar and Hemming took out a patent for it in 1838 and worked it for a short time in London. It was also worked near Paris by Schloesing and Rolland in 1855, but was first successfully used by Ernest Solvay, whose first patent was taken out in 1861 but whose process was first worked on a large scale near Nancy in 1872. The Solvay process was introduced into England in 1874 by Ludwig Mond and John Brunner, whose works at Northwich in Cheshire is still operated by Imperial Chemical Industries.*

In the ammonia-soda process salt brine nearly saturated with common salt is taken and ammonia gas dissolved in it in an iron tower fitted with bubblers. Carbon dioxide is then bubbled under pressure through the ammoniacal brine in a second iron *carbonating tower* (Fig. 146) fitted inside with perforated bubblers, the lower part of the tower being cooled by iron pipes (not shown in the figure) through which cold water circulates. The sodium bicarbonate precipitates and the liquid containing it in suspension is passed to rotating suction filters, on which the bicarbonate is washed with a little water. The mother liquor contains the undecomposed salt and ammonium carbonate and chloride; it is passed to ammonia stills where it is heated with steam and milk of lime to recover the ammonia :



The reaction :



is reversible and usually only about two-thirds of the common salt is converted into bicarbonate, the rest being wasted together with the chlorine

* See Miall, *A History of the British Chemical Industry*, 1931; on the manufacture of alkali, Partington, *The Alkali Industry*, 1925.

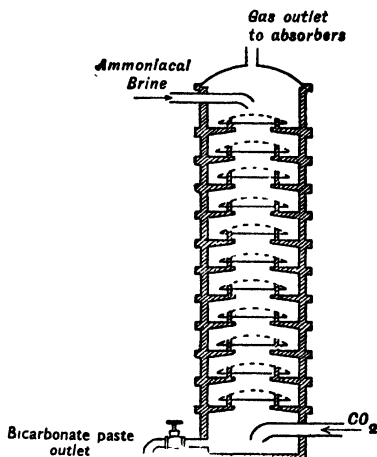


FIG. 146.—Carbonating tower.

of the decomposed salt, which goes to calcium chloride in the ammonia stills.

The sodium bicarbonate from the filters is calcined in closed tubular *calcining pans*, fitted with scrapers which push the solid along the pan. Carbon dioxide is evolved :

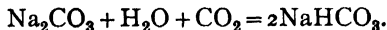


This gas, which is nearly pure ("roaster CO_2 "), is mixed with the scrubbed gas from *limekilns*, where the limestone is burnt mixed with coke to produce lime for the ammonia stills. The mixed gas is passed to the carbonating towers. Sodium carbonate or *soda-ash* issues from the calcining pan. This is nearly pure (99.5 per cent.); it usually contains only a little sodium chloride derived from the mother liquor left in the bicarbonate on the filters.

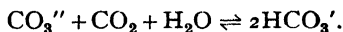
From the soda-ash of the ammonia-soda works, various products may be made. *Washing soda* $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is obtained by dissolving in hot water and crystallising. *Crystal carbonate* $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ is formed by evaporation and separates from the hot solution. *Concentrated soda crystals* $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ are produced by crystallising a hot solution of equimolecular amounts of carbonate and bicarbonate. Caustic soda is made by boiling the solution of the carbonate with lime, as already described.

The ammonia-soda process is more economical and gives a purer product than the Leblanc process.

Sodium bicarbonate.—This salt is produced in large quantities in the ammonia-soda process but is all converted into carbonate, the bicarbonate of commerce being prepared from the latter. A concentrated solution or moist crystals of sodium carbonate when saturated with carbon dioxide give a white crystalline powder of bicarbonate. This may be washed with a little cold water, in which it is sparingly soluble, and dried in the air :



The equation may be written in ionic form as :

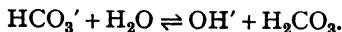


The precipitation is due to the fact that in concentrated solutions the solubility-product $[\text{Na}'] \times [\text{HCO}_3']$ of the salt is exceeded.

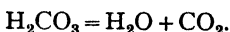
The precipitated bicarbonate is freed by washing from impurities contained in the original carbonate (*e.g.* NaCl), since these are more soluble, and if it is carefully heated in a platinum crucible pure sodium carbonate is produced, which may be used as a standard in volumetric analysis :



The solution of the bicarbonate is slightly hydrolysed and has an alkaline reaction, although this is much feeble than that of the carbonate :

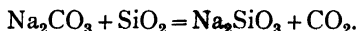


On heating the solution, carbon dioxide is evolved :

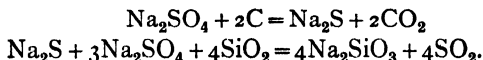


By prolonged boiling practically all the bicarbonate is converted into carbonate, and if crude bicarbonate from the ammonia-soda process is boiled with water, the ammonium salts are decomposed and ammonia is evolved. On recarbonating, almost pure sodium bicarbonate is precipitated and the commercial salt is made in this way.

⤵ **Sodium silicate.**—Sodium silicate (*soluble glass*) is made by melting together sodium carbonate and powdered quartz or pure sand in a reverberatory furnace at a high temperature. Probably various silicates are formed, and the composition may vary from $\frac{2}{3}$ to 4 SiO_2 to 1 Na_2O :



A mixture of sodium sulphate (*salt-cake*) and powdered coal may be substituted for sodium carbonate :



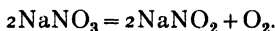
The product is a greenish-blue glass (brown if sodium sulphide is present), which when broken up and heated with water under pressure in autoclaves is slowly dissolved to form a thick solution known as *water glass*, which may contain 2 to 4 molecules of SiO_2 to 1 molecule of Na_2O . It is alkaline, and is used in adding to soap, impregnating wood, weighting silk, as a mordant, in making bricks non-porous, as an adhesive in making cardboard boxes, treating cement floors to reduce dust and abrasion, for preserving eggs, and other purposes. The crystalline *metasilicate* $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ is readily soluble in cold water and is used in laundries.

Sodium nitrate.—Sodium nitrate NaNO_3 can be prepared in the usual way from nitric acid and caustic soda or sodium carbonate, but it occurs in large deposits in the rainless districts of Chile, hence it is often called "Chile saltpetre" or "Chile nitre".

The sodium nitrate in the deposits constitutes from 20 to 50 per cent. in a distinct stratum of earth known as *caliche*. The caliche is crushed and lixiviated in large tanks of water heated by steam. The settled solution is run off to crystallisers, where crude nitrate separates, the mother liquors being run back to the lixiviators. The crystals are washed with a little water and dried in the sun: they contain 95-96 per cent. of

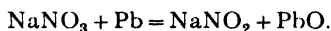
NaNO₃. Most of the export of Chile nitre is used directly as a fertiliser; the remainder is used as a source of potassium nitrate and of nitric acid.

Sodium nitrate crystallises in rhombohedra isomorphous with calcite, resembling cubes, hence it is sometimes called "cubic nitre". It differs from potassium nitrate in being deliquescent. It melts at 316° and at higher temperatures evolves oxygen, leaving sodium nitrite :

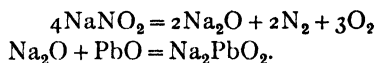


The reduction occurs at a lower temperature in presence of lead, which is oxidised.

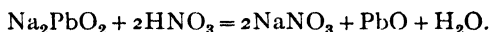
Sodium nitrite NaNO₂ is made by heating sodium nitrate with lead :



The mass is extracted with water and carefully neutralised with nitric acid. Some sodium oxide is formed in the reduction and combines with lead oxide to form a soluble plumbite :



This is precipitated on neutralisation :



The filtered solution is evaporated and crystallised. The crystals are thin flat prisms, slightly yellow in colour and moderately deliquescent. The solution is not alkaline if the salt is pure. Sodium nitrite is used in the manufacture of dyes.

Sodium phosphates.—Ordinary (secondary) **sodium phosphate** (disodium hydrogen phosphate) is prepared by neutralising phosphoric acid with sodium hydroxide or carbonate and evaporating. It forms efflorescent monoclinic crystals Na₂HPO₄·12H₂O, readily soluble in water. The effloresced salt contains 7H₂O. The solution is faintly alkaline.

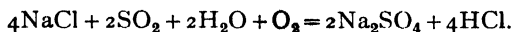
Microcosmic salt or sodium ammonium hydrogen phosphate NaNH₄HPO₄·4H₂O, is formed by dissolving 6 gm. of ammonium chloride and 36 gm. of ordinary sodium phosphate in a little hot water, filtering off the sodium chloride, and crystallising.

The **primary** or **acid sodium phosphate** NaH₂PO₄·H₂O (sodium dihydrogen phosphate) is prepared by adding phosphoric acid to a solution of the ordinary phosphate until a little of the solution no longer precipitates barium chloride, evaporating and crystallising. **Trisodium phosphate** is prepared by dissolving ordinary sodium phosphate and sodium hydroxide in hot water and evaporating ; on cooling, crystals of Na₃PO₄·12H₂O separate, not efflorescent or deliquescent. It has been used under the

name of "tripsa" for softening boiler-water. The calcium bicarbonate is precipitated as carbonate by the alkali formed by hydrolysis, and calcium and magnesium chlorides and sulphates are precipitated as phosphates. The **hexametaphosphate** (p. 519) is now generally used in water-softening.

Sodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$ is obtained by heating the secondary phosphate (p. 518), and **sodium metaphosphate** NaPO_3 by heating the primary phosphate or microcosmic salt (p. 519).

Sodium sulphate.—Anhydrous sodium sulphate Na_2SO_4 occurs native as *thenardite*; *glauberite* is the double salt $\text{CaSO}_4, \text{Na}_2\text{SO}_4$. The efflorescence on brick walls is usually sodium sulphate. Normal sodium sulphate is made in large quantities as *salt-cake* in the first part of the Leblanc process (p. 282). It is also made by the *Hargreaves process*; sulphur dioxide from pyrites burners, air and water vapour are passed over carefully moulded lumps of dry common salt heated in an iron retort, when the following reaction occurs:

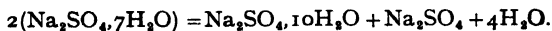


Sodium sulphate is also made from *kieserite* (p. 290) or magnesium sulphate in Stassfurt. This is dissolved in hot water and common salt added. On cooling, Glauber's salt crystallises, as it is the least soluble salt which can be formed from the ions Mg^{++} , Na^+ , SO_4^{--} and Cl^- in the cold solution.

Sodium sulphate crystallises from water as *Glauber's salt* $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$ in large monoclinic prisms which effloresce readily in the air and fall to a white powder of the anhydrous salt.

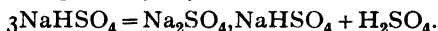
The crystals melt at $32\cdot38^\circ$ and at the same time deposit the anhydrous solid salt, a solution saturated with the latter being formed. The solubility of Glauber's salt reaches a maximum at $32\cdot38^\circ$, since at this temperature the solid in contact with the solution is converted into the anhydrous salt, the solubility of which diminishes with further rise of temperature. The solubility curve (see Fig. 8) consists of two parts meeting in a sharp angle at $32\cdot38^\circ$, the first being the solubility curve of Glauber's salt and the second that of the anhydrous salt.

Glauber's salt readily forms supersaturated solutions. If the supersaturated solution is brought in contact with a minute crystal of Glauber's salt, such as those floating in dusty air, crystallisation begins and Glauber's salt is deposited. But if cooled to 5° it deposits crystals of a metastable *heptahydrate* $\text{Na}_2\text{SO}_4, 7\text{H}_2\text{O}$, which become opaque when touched with a crystal of Glauber's salt owing to decomposition:



Glauber's salt is largely used in the textile industry and in small amounts as a purgative.

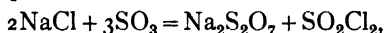
Sodium hydrogen sulphate (acid sodium sulphate or "sodium bisulphate") NaHSO_4 is formed in large prisms by the action of warm concentrated sulphuric acid on anhydrous sodium sulphate. It is formed in the preparation of hydrochloric acid (p. 156). It melts at a much lower temperature than the normal sulphate. A fused mixture or compound of this salt and the normal sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, is formed as a by-product in the manufacture of nitric acid and is known as *nitre-cake*. The hydrate $\text{NaHSO}_4, \text{H}_2\text{O}$ is known. The acid sulphate is decomposed by alcohol into the salt $\text{NaHSO}_4, \text{Na}_2\text{SO}_4$ and free sulphuric acid (dry KHSO_4 is not decomposed by dry alcohol) :



Sodium disulphate (or **pyrosulphate**) $\text{Na}_2\text{S}_2\text{O}_7$ is formed on moderate heating of the acid sulphate :



by the action of sulphur trioxide on common salt :



or (in the pure state) by the action of sulphur trioxide on the normal sulphate :



At a red heat it decomposes into sulphur trioxide and the normal sulphate.

Sodium sulphide, see p. 296. **Sodium sulphite**, see p. 555.

Sodium in analysis.—Sodium compounds give an intense yellow flame, which in the spectroscope shows two yellow lines very close together, known as the D-line. A yellow precipitate of sodium zinc uranyl acetate $\text{NaZn}_2(\text{UO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_6$ is produced by zinc uranyl acetate * in neutral solution, from which potassium salts have been precipitated by zinc perchlorate. White sparingly soluble precipitates of sodium salts are formed with hydrofluosilicic acid, potassium pyroantimoniate or potassium dihydroxytartrate and fairly concentrated solutions of sodium compounds.

The **atomic weight** of sodium has been determined by precipitation of silver nitrate obtained from pure silver with sodium chloride ; by assuming the atomic weights of Ag and Cl the value for Na is found.

POTASSIUM

Occurrence.—Potassium and sodium occur in about the same amounts

* 10 gm. of uranyl acetate UO_2Ac_2 , $2\text{H}_2\text{O}$ and 6 c.c. of acetic acid made up to 50 c.c. form solution A. 30 gm. of zinc acetate ZnAc_2 , $2\text{H}_2\text{O}$ and 6 c.c. of acetic acid made up to 50 c.c. form solution B. Mix A and B and after 48 hours filter.

(see Fig. 17, p. 18), but whereas sodium is found as chloride in the sea and in the earth as rock salt and brine, potassium occurs mostly as a constituent of insoluble rocks and is much less accessible than sodium.

Primary rocks often contain potassium silicate; granite contains about $2\frac{1}{2}$ per cent. of potassium, mainly in the form of *orthoclase feldspar* KAlSi_3O_8 . *Potash mica* or *muscovite* has the formula $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$. Feldspar occurs in granite, gneiss and basalt, and mica in granite and gneiss. During the "weathering" of these rocks, *i.e.* their decomposition by atmospheric carbon dioxide and water assisted by the disintegrating action of frost, the feldspar is decomposed into clay and soluble potassium salts, such as potassium carbonate. The latter are retained by the soil, where they remain available for absorption by the roots of plants. The mechanism of the selective retention of potassium salts by the soil appears to depend on the exchange of potassium for sodium in *zeolites* (see p. 56).

In plants, potassium occurs as salts of organic acids. When plants are burnt these organic salts form potassium carbonate K_2CO_3 , which (since it was formerly prepared by calcining cream of tartar) received the name *salt of tartar*. Large amounts of potassium carbonate are made in Canada, Transylvania and Russia by lixiviating wood ashes with water, evaporating the solution to dryness and calcining the residue in iron pots. The product is *pot-ash* and when purified is known as *pearl-ash*. Sugar beets absorb from the soil considerable amounts of potassium salts, which accumulate in the molasses, known as *vinasse* or *schlempe*. This is evaporated on open hearths and splashed by paddles in the fire gases (Porion furnace); the syrup burns, leaving a residue of potassium carbonate. The *vinasse* may also be distilled in iron retorts, when methyl chloride and trimethylamine are formed.

The perspiration (*suint*) of the sheep is rich in potassium salts. If raw wool is washed with water, the brown liquid evaporated and the residue calcined, about 5 parts of potassium carbonate remain per 100 of wool. This is a limited source of potassium salts.

Potassium salts occur in small quantities only in the sea and are absorbed in marine plants, from the ashes of which (*kelp*) they may be extracted.

Although potassium compounds are widely distributed, *e.g.* as feldspar, comparatively few workable mineral deposits of salts occur. The principal are at Stassfurt in Saxony and near Mulhouse in Alsace, and in lesser amounts near Kalusz in Poland, Carlsbad in New Mexico, in Eastern Galicia, Searle's Lake (California), Cardona in Spain, Tunis, the Dead Sea (Palestine) and Elton Lake in the Urals.

The Alsatian and Galician deposits contain *sylnite* or *sylnite*, a mixture of sodium and potassium chlorides. The Alsatian deposit consists of two strata, the upper with 35 to 40 per cent. KCl and the lower with 24 to 32 per cent. KCl.

The Stassfurt deposits contain several minerals, some of which are

double salts containing potassium. The most important is potassium magnesium chloride, $\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$, called *carrollite*, which is a source of potassium and magnesium salts. Less important is *kainite*, $\text{KCl}, \text{MgSO}_4, 3\text{H}_2\text{O}$.

Potassium.—The metal can be prepared in a similar way to sodium by the electrolysis of fused potassium hydroxide, although the operation is difficult to carry out and the electrolysis of fused potassium chloride is preferable. It comes into the market in small spheres, kept under petroleum.

It may be obtained on a small scale by electrolysis of a fused mixture of equimolecular proportions of potassium chloride and calcium chloride in a porcelain crucible provided with two carbon electrodes, and heated with a bunsen burner placed on the anode side, so that a solid crust forms over the cathode. A globule of potassium forms under the crust. The pure metal is best obtained by heating potassium chloride with calcium in a vacuum.

Metallic potassium was formerly prepared by strongly heating a mixture of the carbonate with charcoal in an iron bottle, and cooling the vapour rapidly in a flat iron condenser: $\text{K}_2\text{CO}_3 + 2\text{C} = 2\text{K} + 3\text{CO}$. Unless the cooling is rapid, reaction of potassium with carbon monoxide occurred, with the formation of a yellow compound $\text{C}_6\text{O}_6\text{K}_6$, which on exposure to moist air forms very explosive substances.

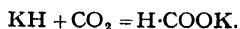
Potassium can be prepared by the electrolysis of potassium cyanide; by heating potassium hydroxide or sulphide with iron, magnesium, or aluminium; or by heating calcium carbide with potassium fluoride.

Potassium is a very light, soft metal, with a silver-white colour. It forms a green vapour. The metal is not acted upon by perfectly dry oxygen, but is rapidly corroded in moist air, becoming covered at first with a blue film. Potassium is chemically more energetic than sodium. It acts violently on water, the liberated hydrogen burning with a lilac-coloured flame. A fused globule of potassium hydroxide remains floating on the water; as it cools and touches the water, it explodes with a sharp crack. Heated potassium decomposes nearly every gas which contains oxygen; it also decomposes the oxides of boron and silicon, and the chlorides of magnesium and aluminium, on heating, with liberation of the elements.

An alloy of sodium and potassium is liquid at room temperature and resembles mercury, but is very easily oxidised with evolution of heat and light on exposure to air. Potassium is feebly radioactive, one isotope of it emitting β -rays.

Potassium hydride.—Potassium hydride K^+H^- is a white crystalline solid formed by heating potassium in hydrogen. It ignites spontaneously in

chlorine or oxygen; moist carbon dioxide at room temperature converts it into potassium formate:



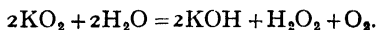
Potassium chloride.—This salt KCl occurs in cubic crystals as *sylvine*. It is easily soluble in water, the solubility increasing almost linearly with temperature (*cf.* NaCl). It is made for use as a fertiliser from Stassfurt carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

The crude carnallite is heated with mother liquor containing magnesium chloride, when it dissolves. The solution is filtered and cooled, when crude potassium chloride crystallises out, leaving a mother liquor containing the magnesium chloride of the carnallite. The potassium chloride is then purified by washing and recrystallisation.

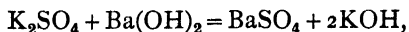
Potassium bromide KBr and **potassium iodide** KI are prepared as previously described (pp. 181, 188).

If aqueous hydrofluoric acid is neutralised with potassium hydroxide and the liquid evaporated in a platinum dish, cubic crystals of **potassium fluoride** KF are obtained. If to the neutralised liquid a further equal volume of hydrofluoric acid is added and the liquid evaporated in a platinum dish, crystals of **potassium hydrogen fluoride** KHF_2 or $\text{KF} \cdot \text{HF}$, called **Fremy's salt**, are obtained. This may be dried by gentle heating and is relatively stable. On heating more strongly it decomposes: $\text{KHF}_2 = \text{KF} + \text{HF}$. The salts KH_2F_3 and KH_3F_4 are also known.

Oxides of potassium.—**Potassium monoxide** K_2O is light yellow and is prepared in a similar manner to the sodium compound and has similar properties. **Potassium dioxide** KO_2 is obtained as a chrome-yellow solid by burning the metal in excess of oxygen or air. It oxidises carbon monoxide to dioxide below 100° , and is decomposed by water:



Potassium hydroxide.—Potassium hydroxide is prepared in a similar way to sodium hydroxide, which it resembles closely. It is made on the large scale by the electrolysis of potassium chloride solution and is used in the manufacture of *soft soap* (potassium salts of oleic, palmitic and stearic acids). The pure hydroxide is best prepared by adding powdered potassium sulphate to a hot saturated solution of barium hydroxide:



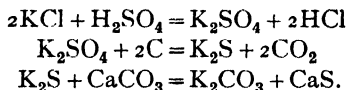
or by the action of water on potassium amalgam. The solutions attack glass, and should be decanted (not filtered) and evaporated in silver, nickel or iron dishes. Platinum is attacked by fused alkalis.

Potassium hydroxide is more soluble than sodium hydroxide both in

water and in alcohol, and the alcoholic solution ("alcoholic potash") is used as a reagent; it becomes brown owing to oxidation of the alcohol. Potassium hydroxide forms a crystalline hydrate $\text{KOH} \cdot 2\text{H}_2\text{O}$.

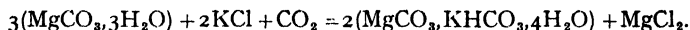
The impure commercial caustic potash containing chloride, carbonate and sulphate may be purified by dissolving in alcohol, decanting from the impurities, evaporating the solution in a silver dish and fusing the residue. It is sold as "pure by alcohol" but may contain a little potassium acetate formed from the alcohol.

Potassium carbonate.—Potassium carbonate K_2CO_3 is made from wood-ash (p. 290), and when purified is called *pearl-ash*. It can be made from potassium chloride by a modification of the Leblanc process; the chloride is first decomposed with sulphuric acid to form potassium sulphate as in the salt-cake process, and the sulphate is then heated with coal and limestone as in the black-ash process:



It is usually made from potassium chloride by **Precht's process**.

A concentrated solution of potassium chloride is mixed with solid hydrated magnesium carbonate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, and carbon dioxide (limekiln gas) is passed into the suspension. A solid compound of potassium bicarbonate and magnesium carbonate is precipitated and a solution of magnesium chloride is formed:

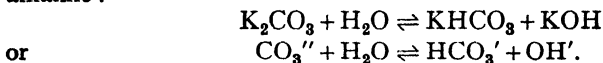


The solid double carbonate is then stirred with water and magnesium oxide at 40° , when a solution of potassium carbonate and a residue of hydrated magnesium carbonate are formed:



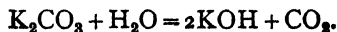
The solution of potassium carbonate is filtered and evaporated.

Potassium carbonate is a white deliquescent solid, very easily soluble in water to form a solution which, on account of hydrolysis, is strongly alkaline:

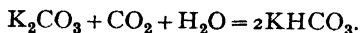


Crystalline hydrates $\text{K}_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$ and $2\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$, are known.

Potassium carbonate melts at a red heat and it forms a more easily fusible mixture ("fusion mixture") with sodium carbonate. It is decomposed by steam at a red heat:



A saturated solution of potassium carbonate readily absorbs carbon dioxide and deposits crystals of **potassium hydrogen carbonate** or **bicarbonate**:



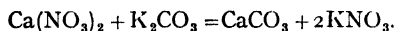
This salt is easily prepared by passing carbon dioxide over moistened potassium carbonate and drying on a porous plate. It is much less soluble in water than the normal carbonate, but is more soluble than sodium bicarbonate. The recrystallised bicarbonate may be used in preparing pure potassium carbonate, since it decomposes on heating :



Potassium nitrate.—Potassium nitrate KNO_3 , called *nitre* or *saltpetre* (Latin, *sal petrae*), may be prepared by neutralising dilute nitric acid with potassium hydroxide or carbonate, evaporating and crystallising. It is manufactured for use in making gunpowder, and small amounts are also used in pickling meat, *e.g.* hams.

An old method of manufacturing **saltpetre** which is still used in India is in the so-called *nitre plantations*.

Soil containing decomposing nitrogenous organic matter such as urine is mixed with lime or calcium carbonate, such as old mortar, when calcium nitrate $\text{Ca}(\text{NO}_3)_2$ is produced, probably from the oxidation of ammonia formed by the decomposition of organic matter in the presence of feeble alkalis, by the activity of micro-organisms present in soil (see p. 476). The material is lixiviated and a solution containing calcium nitrate is obtained which is boiled with wood-ashes (containing potassium carbonate):

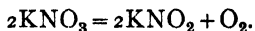


The filtrate on evaporation deposits **saltpetre**, which is purified by recrystallisation.

The cheaper sodium nitrate is converted into potassium nitrate by dissolving potassium chloride in a little hot water and adding sodium nitrate. Sodium chloride, the least soluble salt formed from the four ions K^+ , Na^+ , NO_3^- , Cl^- , is deposited from the hot liquid, since its solubility is not much increased by rise of temperature (see Fig. 8) ; if the mother liquor is allowed to cool, potassium nitrate crystallises out, since it is the least soluble salt at lower temperatures. It is recrystallised from water.

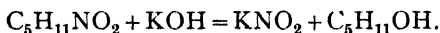
The process may be illustrated by dissolving 11.5 gm. of NaNO_3 and 10 gm. of KCl in 10 c.c. of boiling water; white granular NaCl remains; on filtering through a hot-water funnel, the filtrate on cooling deposits crystals of KNO_3 , which may be recrystallised.

Potassium nitrate usually crystallises in large anhydrous rhombic prisms, but if the solution is slowly evaporated on a watch-glass, rhombohedra isomorphous with sodium nitrate and with calcite are deposited. Nitre melts at 336° and at a higher temperature it evolves oxygen :



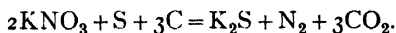
The fused salt is a powerful oxidising agent ; sulphur, charcoal and phosphorus take fire on it and burn brilliantly, with formation of potassium sulphate, carbonate and phosphate. Potassium chlorate is a more powerful oxidising agent than potassium nitrate.

Potassium nitrite is made in the same way as sodium nitrite (p. 287), but as it does not crystallise well it is fused and cast into sticks. It is yellowish in colour and the crystals are tiny short prisms very soluble in water, so that it cannot be purified by recrystallisation. The pure salt (which is not deliquescent) is made by decomposing amyl nitrite with alcoholic potash and evaporating :



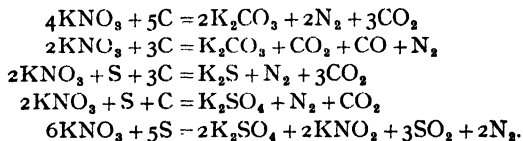
Gunpowder.—Most of the potassium nitrate of commerce is used in making gunpowder.

Gunpowder is an intimate mixture of finely powdered nitre, wood-charcoal (carbonised at a low temperature) and sulphur. The proportions of the constituents and the main products of combustion correspond roughly with the following equation :



The proportions of nitre, carbon and sulphur corresponding with this equation are 75, 13 and 12, respectively. Carbon monoxide is also evolved in the explosion and the residue contains some potassium carbonate and sulphate.

The gaseous product is mostly carbon dioxide, carbon monoxide and nitrogen, whilst the solid product (including that in the dense smoke) is mainly potassium carbonate, potassium sulphate and potassium sulphide. The *principal* reactions in the explosion may be represented by the equations:



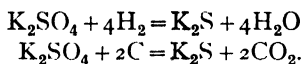
Potassium phosphates.—Ordinary potassium phosphate is the primary potassium dihydrogen phosphate KH_2PO_4 (ordinary sodium phosphate is

Na_2HPO_4). This is prepared by adding potassium hydroxide solution to phosphoric acid till neutral to phenolphthalein, and evaporating : it forms deliquescent crystals. The tertiary phosphate K_3PO_4 is formed with excess of alkali and is very soluble ; the secondary phosphate K_2HPO_4 is difficult to crystallise.

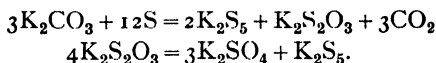
Potassium and sodium sulphides.—Potassium and sodium burn when heated in sulphur vapour, forming mixtures of sulphides. By using excess of metal and heating the product in a vacuum, the pure monosulphides K_2S and Na_2S remain in cubic crystals.

The monosulphides readily combine with more sulphur, either on fusion or by boiling the solutions with sulphur, to form polysulphides Na_2S_x and K_2S_x ($x = 2$ to 6). These contain chains of sulphur atoms linked by single bonds, $-\text{S}-\text{S}-$ and $-\text{S}-(\text{S})_n-\text{S}-$.

The monosulphides Na_2S and K_2S are obtained by passing hydrogen over the heated sulphates, and in a less pure form by heating the sulphates with excess of carbon :

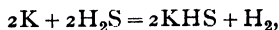


By fusing potassium carbonate with sulphur, a liver-coloured mass is obtained, known as *liver of sulphur* (*hepar sulphuris*). It contains polysulphides of potassium, together with potassium sulphate : the pentasulphide and thiosulphate are first formed but most of the thiosulphate is decomposed by heat :

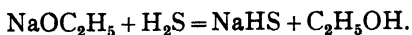


A solution of liver of sulphur is used in gardening to combat mildew and insect pests.

If a solution of sodium or potassium hydroxide is saturated with hydrogen sulphide and evaporated, the hydrosulphides $\text{NaHS}\cdot 2\text{H}_2\text{O}$ or $\text{NaHS}\cdot 3\text{H}_2\text{O}$ and $2\text{KHS}\cdot \text{H}_2\text{O}$ crystallise out. The anhydrous compounds are obtained by heating the metals in hydrogen sulphide :

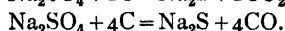
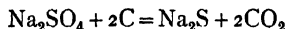


or by the action of hydrogen sulphide on solutions of sodium or potassium ethoxides in ethyl alcohol :



If a solution of alkali hydroxide is saturated with hydrogen sulphide, an equal volume of the alkali is added, and the solution is evaporated, the monosulphides $\text{K}_2\text{S}\cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ separate in colourless crystals.

Sodium sulphide is made technically by fusing salt-cake with powdered coal in a revolving furnace :



The product is lixiviated with water, evaporated and crystallised. It is used in removing hair from skins and in making sulphur dyes. The residual sulphide liquor is treated with sodium carbonate and sulphur dioxide to make thiosulphate :

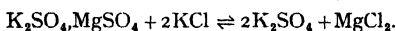


By boiling alcoholic solutions of the hydrosulphides with sulphur, **potassium pentasulphide** K_2S_5 and **sodium tetrasulphide** Na_2S_4 are obtained. K_2S_5 forms bright orange-red crystals giving a deep-orange solution which becomes darker on heating. Na_2S_4 forms dark-yellow crystals giving a deep-orange solution which also becomes darker on heating. **Sodium disulphide** Na_2S_2 is obtained by adding sodium to an alcoholic solution of Na_2S_4 and forms bright-yellow microscopic crystals, giving a deep-yellow solution which does not darken on heating.

Potassium sulphate.—When dilute sulphuric acid is neutralised with potassium hydroxide or carbonate and the solution evaporated, *anhydrous* rhombic prisms of **potassium sulphate** K_2SO_4 separate. These are not very soluble in water ; the solubility increases almost linearly with the temperature (Fig. 8).

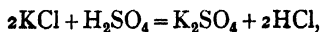
Potassium sulphate occurs in large quantities in double salts of the Stassfurt potash deposits : *schönite* $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, and *kainite* $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$.

If kainite is dissolved in hot water it breaks up into its constituent ions $\text{K}^+, \text{Mg}^{++}, \text{SO}_4^{--}, \text{Cl}^-$. By fractional crystallisation, those salts separate first (including double salts) with which the solution first becomes saturated (van't Hoff). From warm solutions the double salt *schönite* first separates, since it is least soluble, and magnesium chloride remains in solution. If the *schönite* is digested with a solution of potassium chloride (occurring at Stassfurt as *sylvine*), the following reaction occurs :



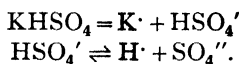
The sparingly soluble potassium sulphate separates first, followed by *carnallite* $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, from which potassium and magnesium chlorides can be prepared.

Potassium sulphate is made in smaller amounts by heating concentrated sulphuric acid with potassium chloride :



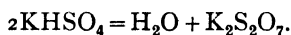
and as a by-product in the manufacture of potassium dichromate and permanganate. It is used in the preparation of potash alum and as a fertiliser, especially for tobacco, since it is fusible with difficulty and gives a suitable ash.

When potassium sulphate is heated with an equivalent of concentrated sulphuric acid it dissolves, forming **potassium hydrogen sulphate** KHSO_4 ("potassium bisulphate" $\text{K}_2\text{O}, 2\text{SO}_3, \text{H}_2\text{O}$ or "acid potassium sulphate") (Rouille, 1754). This is easily fusible. It is obtained as a by-product in the laboratory preparation of nitric acid. It is readily soluble in water, the solution having a strongly acid reaction :



On evaporation the solution (in accordance with van't Hoff's rule) deposits the normal sulphate K_2SO_4 , which is the salt with which it first becomes saturated. The residual solution contains free sulphuric acid. From it on cooling a **trisulphate** $\text{K}_2\text{SO}_4, \text{KHSO}_4$ or $\text{K}_2\text{O}, 3\text{SO}_3, \text{H}_2\text{O}$ deposits, and finally KHSO_4 . The compounds $\text{K}_2\text{SO}_4, 3\text{KHSO}_4$ and $\text{K}_2\text{SO}_4, 6\text{KHSO}_4$ are also known.

At a red heat potassium hydrogen sulphate loses water and forms **potassium disulphate** (or **pyrosulphate**) :



At higher temperatures this evolves sulphur trioxide :



It is used to attack refractory minerals in analysis, since it behaves like sulphuric acid of high boiling point. Thus chromite FeCr_2O_4 is converted into ferrous and chromic sulphates, FeSO_4 and $\text{Cr}_2(\text{SO}_4)_3$, although it is not attacked by boiling sulphuric acid. Since loss of water on heating KHSO_4 is incomplete even in a vacuum, the pure pyrosulphate is best obtained from sulphur trioxide and potassium sulphate :



Potassium in analysis.—Potassium salts form sparingly soluble salts with perchloric, hydrofluosilicic, chloroplatinic, phosphotungstic, tartaric and picric acids, and with sodium cobaltinitrite. Potassium iodide is not precipitated by chloroplatinic acid. Potassium hydrogen tartrate is precipitated only in solutions containing no mineral acid ; it (as well as the chloroplatinate) is precipitated more easily by adding alcohol and scratching the tube with a glass rod. The lilac flame coloration and the spectrum are also useful as tests.

The atomic weight of potassium was found by a method similar to that used for sodium (p. 288).

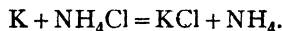
AMMONIUM

Ammonium.—Ammonia readily combines with acids to form salts. Lavoisier, and later Dumas (1828), regarded these as compounds of ammonia with acids, *e.g.* ammonia hydrochloride $\text{NH}_3\cdot\text{HCl}$. Davy (1808) and Ampère (1816) supposed that the salts contain the **ammonium radical** NH_4 , which behaves as an alkali-metal. Sal ammoniac is *ammonium chloride* NH_4Cl , analogous to potassium chloride KCl . This view was favoured by Berzelius in 1820.

The ammonium theory had its origin in the discovery of **ammonium amalgam**, obtained independently in 1808 by Seebeck in Jena and by Berzelius and Pontin in Stockholm. If a solution of ammonium chloride is electrolysed with a mercury cathode (Fig. 105) the mercury swells up in a curious manner, forming a soft pasty mass which rapidly decomposes, evolving hydrogen and ammonia in the ratio of 1 vol. to 2 :



Davy in 1808 confirmed this observation and showed that the ammonium amalgam could also be obtained by the action of potassium amalgam on a solution of ammonium chloride :

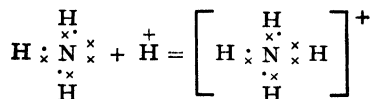


If a little sodium amalgam is added to a cold solution of ammonium chloride, the amalgam swells up and forms a spongy mass. If this is put into water, bubbles of hydrogen are evolved and the liquid smells of ammonia.

Seely (1870) found that ammonium amalgam compressed in a tube under a piston obeys Boyle's law and concluded that it was simply a froth of hydrogen and ammonia gases in mercury. Ammonia, however, is very soluble in water and other experiments favour the existence of ammonium in the amalgam. Although the amalgam does not reduce solutions of ferric chloride or copper sulphate at the ordinary temperature, it reduces solutions of copper, cadmium, zinc and even barium salts at 0° . The voltage required to deposit sodium on a mercury cathode is similar to that required in the formation of ammonium amalgam. Ammonium amalgam is also formed by the action of sodium amalgam on ammonium chloride dissolved in anhydrous liquid ammonia. Metallic sodium and potassium dissolve in anhydrous liquid ammonia to form deep blue solutions which are conductors of electricity.

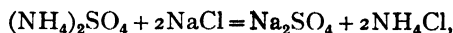
The ammonium salts were formerly regarded as containing 5-valent nitrogen, *e.g.* $(\text{H}_4)\equiv\text{N}-\text{Cl}$, but it is now considered that the positive ammonium ion is formed by the addition of the neutral ammonia molecule to the hydrogen ion (proton), which remains univalent so that the whole

ammonium ion is also univalent. The proton is linked by the lone pair of electrons on the nitrogen atom:



The four hydrogens are attached to the nitrogen at the corners of a tetrahedron with nitrogen at the centre, the valencies being in the same directions as those from a carbon atom (Mills and Warren, 1925). In ammonium salts the NH_4 ions form a lattice with negative ions (Fig. 56).

Ammonium chloride.—This compound occurs in volcanic gases. It is known as *sal ammoniac* and is prepared by neutralising ammonia with hydrochloric acid and evaporating, also by subliming a mixture of ammonium sulphate with common salt:

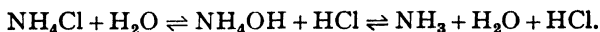


by heating in a cast-iron basin provided with an iron dome having a small hole at the top. The cake of ammonium chloride which sublimes into the dome is broken up and forms tough fibrous irregular lumps, often stained in yellow patches with ferric chloride. An imitation of the sublimed product is made by strongly compressing the powdered salt; *voltoids*, used in batteries, are small tablets prepared by compression.

Ammonium chloride is prepared in ammonia-soda works by crystallising the liquors from the bicarbonate filters, which contain NH_4Cl , NaCl and CaCl_2 , and drying the salt with hot air.

Ammonium chloride crystallises in feathery growths consisting of aggregates of small octahedra or other forms of the regular system, so that the crystals look like crystals of the hexagonal or tetragonal system. From a solution containing urea it crystallises in cubes.

The salt is readily soluble in water and a considerable lowering of temperature results. It is very sparingly soluble in absolute alcohol. The aqueous solution is only slightly hydrolysed and is neutral, but ammonia escapes on boiling, leaving a distinctly acid liquid:

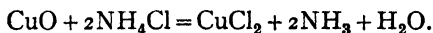


Ammonium chloride vapour is practically completely dissociated:

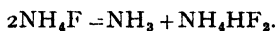


According to H. B. Baker, when the salt is carefully dried over P_2O_5 it gives the normal vapour density corresponding with NH_4Cl , but this result

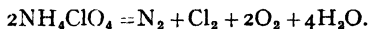
has been called in question by Rodebush and Michalek (1929). The dissociation on heating explains the action of ammonium chloride as a flux in soldering: the metallic oxides are converted into volatile chlorides by the hydrochloric acid, and a clean metal surface is left, *e.g.*:



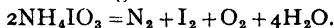
Ammonium fluoride NH_4F , **bromide** NH_4Br and **iodide** NH_4I are obtained by neutralising the corresponding acids with ammonia. The fluoride decomposes on fusion to form the acid fluoride:



Ammonium chlorate NH_4ClO_3 is unstable and spontaneously explosive; even solutions may explode violently on evaporation. The **perchlorate** NH_4ClO_4 is more stable but is endothermic and deflagrates with a yellow flame over 200° :

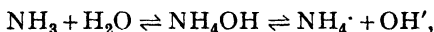


The **iodate** decomposes on heating:

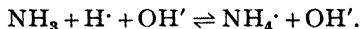


Ammonium hydroxide.—Although crystalline solids of the compositions $2\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$ are known (p. 468), it is doubtful if they are ammonium oxide $(\text{NH}_4)_2\text{O}$ and ammonium hydroxide NH_4OH , respectively.

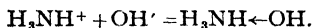
It is sometimes supposed that aqueous ammonia contains ammonium hydroxide, which is a weak base:



but its general properties can be explained by supposing that the ammonia withdraws hydrogen ions from the water to form ammonium ions, leaving the hydroxyl ions of the water which cause the alkaline reaction *:



Ammonia is a weak base and this has been explained by supposing that the lone pair of electrons on the hydroxyl oxygen can co-ordinate (p. 264) with a hydrogen of the ammonium ion to form unionised ammonium hydroxide:



A quarternary ammonium hydroxide, *e.g.* tetramethyl ammonium hydroxide, is a strong base since its radical has no hydrogen with which the hydroxyl oxygen can co-ordinate: $(\text{CH}_3)_4\text{N}^+ + \text{OH}'$.

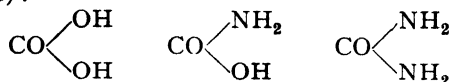
Ammonium carbonates.—Commercial ammonium carbonate or *sal volatile* is obtained by heating a mixture of chalk and sal ammoniac or ammonium sulphate in an iron retort with a lead receiver, into which the salt sublimes. The product is resublimed after the addition of a little

* See, however, Moore and Winmill, *J. Chem. Soc.*, 1912.

water, and comes into the market as a white semi-transparent fibrous mass covered on the outside with a white opaque powder of the bicarbonate NH_4HCO_3 , and smelling strongly of ammonia.

The commercial carbonate is a compound of the bicarbonate and **ammonium carbamate** $\text{NH}_4\text{O}\cdot\text{CO}\cdot\text{NH}_2$, with some **normal carbonate** $(\text{NH}_4)_2\text{CO}_3$.

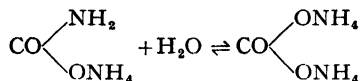
Carbamic acid is the monoamide of carbonic acid, the diamide being urea (*carbamide*) :



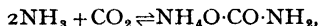
If commercial ammonium carbonate is treated with alcohol the carbamate dissolves leaving the bicarbonate; on exposure to air the carbamate slowly volatilises, leaving the bicarbonate as a white powder. The bicarbonate can be crystallised; at 60° it decomposes:



although at the ordinary temperature it does not smell of ammonia. Commercial ammonium carbonate can be used as a baking powder since it volatilises completely on heating. If it is gently warmed with concentrated ammonia solution a **sesqui-carbonate** $2\text{NH}_4\text{HCO}_3, (\text{NH}_4)_2\text{CO}_3, \text{H}_2\text{O}$ is obtained in crystals. The **normal carbonate** $(\text{NH}_4)_2\text{CO}_3$ is said to be obtained by digesting *sal volatile* for two hours with concentrated aqueous ammonia at 12° , and drying between filter paper the crystalline powder remaining, which is $(\text{NH}_4)_2\text{CO}_3, \text{H}_2\text{O}$. It is formed when the carbamate is dissolved in water:



so that when the commercial carbonate is dissolved in ammonia solution the normal carbonate is formed. The carbamate is deposited when 2 vols. of ammonia gas and 1 vol. of CO_2 are mixed:



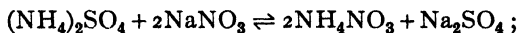
and on heating it dissociates into these constituents.

Synthetic **urea** is made by heating a mixture of ammonia gas, carbon dioxide and a little water under pressure at 135° ; ammonium carbamate is first formed and then loses water:

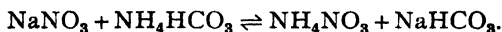


Ammonium nitrate.—This salt was first prepared by Glauber and called *nitrum flammans* (since it explodes when suddenly heated). It is obtained by neutralising nitric acid with ammonia or ammonium carbonate. On the large scale it is made (1) by passing ammonia gas into 60 per cent. nitric acid; (2) by the double decomposition of calcium nitrate and ammonium carbonate or sulphate in solution; (3) by the

double decomposition of ammonium sulphate and sodium nitrate in solution :



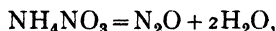
(4) by using sodium nitrate instead of common salt in the ammonia-soda process :



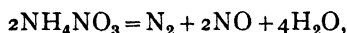
Another method of preparation is described on p. 485.

The salt exists in five crystalline forms, with definite transition temperatures. The melting point of the anhydrous salt is 169.6° , that of the ordinary salt containing a little moisture is 165° . The transition at 84.2° is accompanied by an expansion which may break a glass vessel in which the salt has solidified.

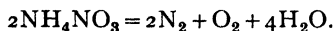
Ammonium nitrate is used in the preparation of nitrous oxide (p. 488) :



and as a constituent of explosives. It deflagrates with a yellow flame above 250° :



and at higher temperatures it detonates :



A mixture (*amatol*) of 80 parts of ammonium nitrate and 20 parts of trinitrotoluene is an explosive.

Ammonium nitrite NH_4NO_2 is obtained as an explosive deliquescent solid by passing " N_2O_3 " gas over solid ammonium carbonate in a cooled tube, dissolving in alcohol, and precipitating with ether.

A solution for the preparation of nitrogen is made by mixing sodium nitrite with ammonium chloride or sulphate in solution.

The ammonium phosphates $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_3\text{PO}_4$ are formed from ammonia and phosphoric acid. *Microcosmic salt* is described on p. 286.

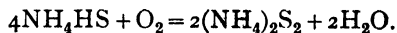
Ammonium sulphides.—The formation of colourless needles and plates of **ammonium hydrosulphide** NH_4HS by mixing equal volumes of ammonia and hydrogen sulphide was described by Bineau in 1838 and confirmed by Bloxam in 1893.

Bineau in 1839 stated that a mixture of 2 vols. of ammonia with 1 vol. of hydrogen sulphide at -18° gave mica-like crystals of ammonium monosulphide $(\text{NH}_4)_2\text{S}$, but Bloxam found that these crystals always contain ammonium hydrosulphide, and although he says he obtained the monosulphide by carefully adjusting the volumes of the reacting gases

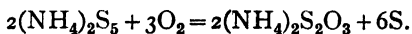
and their rates of flow, the product was probably contaminated with hydrosulphide (Thomas and Riding, 1923).

The pure hydrosulphide is precipitated in fine needles on passing dry ammonia and dry hydrogen sulphide alternately into dry ether. It dissociates rapidly and can be kept only in sealed vessels.

When hydrogen sulphide is passed into concentrated (0.880) ammonia solution diluted with four times its volume of water, a solution of the hydrosulphide is formed. The normal sulphide does not appear to exist in solution. The freshly prepared solution of the hydrosulphide is colourless, but rapidly oxidises on exposure to air and becomes yellow owing to separation of sulphur, which dissolves in the excess of hydrosulphide to form yellow polysulphides $(\text{NH}_4)_2\text{S}_x$:

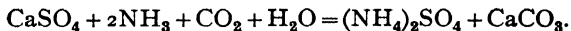


The same *yellow ammonium sulphide* is obtained by digesting flowers of sulphur with the solution of the hydrosulphide : the main product appears to be $(\text{NH}_4)_2\text{S}_5$, which is known in the solid state. On prolonged exposure to air the solutions deposit sulphur, and form a colourless solution containing **ammonium thiosulphate** :



Ammonium sulphate.—Ammonium sulphate is manufactured by passing ammonia gas into 60 per cent. sulphuric acid.

Instead of using sulphuric acid, ammonia gas may be absorbed in a suspension of calcium sulphate (calcined gypsum) and carbon dioxide passed into the liquid, when calcium carbonate is precipitated and a solution of ammonium sulphate is formed :



Ammonium sulphate forms large transparent crystals isomorphous with potassium sulphate and very soluble in water. On heating powdered ammonium sulphate it loses ammonia even below 100° , and at 300° is completely converted into molten **ammonium hydrogen sulphate** which melts at 140° after solidification :



At higher temperatures, decomposition with evolution of sulphur dioxide and nitrogen occurs. The acid sulphate is also obtained in deliquescent crystals by dissolving the normal sulphate in hot concentrated sulphuric acid and cooling.

Odd series or sub-group b of group I.—This sub-group, as is seen from the table on p. 252, contains the metals copper, silver and gold. These metals, which occur in nature in the free state or are easily formed by reduction of their compounds, were the earliest known. Although they

occur in the same group as the alkali metals, the sole similarity is the existence of compounds MX , in which the metals are univalent. Coordination compounds containing bivalent silver are known (p. 327). Copper forms a series of compounds CuX_2 in which it is bivalent, and gold a series AuX_3 in which it is trivalent. Unlike the alkali metals, copper, silver and gold readily form complex compounds in which the metal may be present either in the positive radical, *e.g.* $[Cu(NH_3)_4]SO_4$ or in the negative radical, *e.g.* $K[Ag(CN)_2]$.

Gold, with the highest atomic weight, differs in many respects from the other members of the group; this type of anomaly occurs elsewhere in the periodic table. Gold in many ways resembles platinum. Copper also shows closer relationship with mercury, which forms mercurous and mercuric compounds, than with silver or gold, although the cuprous salts resemble those of silver. Cuprous and silver chlorides are both white insoluble substances, dissolving readily in ammonia. Although silver chloride is quite stable, cuprous chloride is readily oxidised to the cupric compound. The sulphides of copper and silver are isomorphous; the mineral *copper glance*, consisting chiefly of cuprous sulphide Cu_2S , contains silver sulphide Ag_2S in varying amounts.

The table on p. 263 shows that the atoms of copper, silver and gold all contain an inner group of 18 electrons and one valency electron outside. The elements, like the alkali metals in sub-group *a*, can behave as univalent when this valency electron is lost or shared, but they also show valencies of 2 and 3.

When copper, silver and gold function with higher valencies (2 and 3), electrons must be brought out from the inner group of 18, which is then left as an incomplete group (17 or 16).

CHAPTER XXII

COPPER, SILVER AND GOLD

COPPER

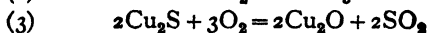
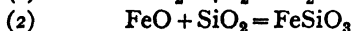
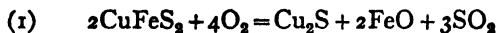
History.—Copper ores are easily reduced and the metal was therefore used in very early times, the oldest specimens of cast copper from Egypt and Babylonia dating to *c.* 4000 B.C. It appears later in the form of its alloy bronze, which contains copper and tin. Working in bronze was practised by the Sumerians at Ur in 3500 B.C. and in Egypt at least as early as 2500 B.C.

Occurrence.—*Native copper* occurs in Sweden, the Ural mountains and in large quantities in America, near Lake Superior. It usually contains small quantities of silver, also bismuth and lead. Cuprous oxide Cu_2O occurs as *cuprite* (or *red copper ore*); cupric oxide CuO occurs in smaller amounts as *tenorite* or *melaconite*. Compounds of the carbonate and hydroxide occurring native are the bright-green *malachite* $\text{CuCO}_3, \text{Cu}(\text{OH})_2$ and the deep-blue *azurite* (or *chessylite*) $2\text{CuCO}_3, \text{Cu}(\text{OH})_2$, which are used in works of art. In combination with sulphur alone, copper occurs in relatively small amounts as *chalcocite* or *copper glance* Cu_2S and *covellite* or *indigo copper* CuS , both probably formed by reduction of the sulphate by organic matter. The commonest ores of copper are *copper pyrites* or *chalcopyrite* CuFeS_2 and *bornite* (*erubescite* or *variegated copper ore*) Cu_3FeS_3 , *i.e.* sulphides of copper and iron. Copper is extracted by the "wet process" from burnt cuprous pyrites used in making sulphuric acid (p. 306), and also from drainage water from stocks of such pyrites. Large quantities of copper now come from the Belgian Congo and Northern Rhodesia. Most of the copper now smelted in America is from ore concentrated by "froth flotation" (p. 269).

Copper occurs in the red colouring matter (*turacin*) of the feathers of the plantain-eater (*Touracus*), and in the *haemocyanin* of the blood of the cuttlefish, which acts like haemoglobin as an oxygen carrier but is blue in arterial and colourless in venous blood. Minute quantities of copper occur in plants, especially in green peas.

Metallurgy of copper.—Native copper is melted with a flux and refined. Oxides (*e.g.* cuprite) and carbonates (*e.g.* malachite) are reduced by heating with carbon. Sulphide ores, *e.g.* copper pyrites CuFeS_2 , from

which a large amount of copper is obtained, are smelted by a somewhat complicated process. The separation of the iron and sulphur from the copper in the ore is difficult, since sulphur has a greater affinity for copper than for iron. The essential part of the process is to get rid of the iron by oxidation as ferrous silicate in the slag and leave the copper as cuprous sulphide. This on roasting in air is partly converted into cuprous oxide, which reacts with the remaining sulphide to form metallic copper :



The ore is first roasted in a large flat furnace, being raked on the hearth to expose a large surface to the air. Part of the copper and iron are oxidised and arsenic is volatilised as oxide. The roasted ore is then heated in a reverberatory furnace (Fig. 147) with silica. In the furnace

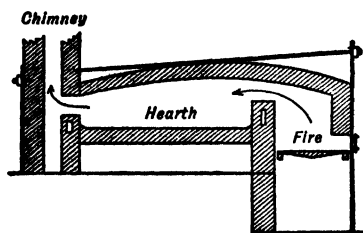


FIG. 147.—Reverberatory furnace.

In the original "Welsh process", the blocks of fine metal were roasted in a current of air on the hearth of a reverberatory furnace, when reactions (3) and (4) occurred. In modern practice the molten white metal is charged into a Bessemer converter and a blast of air sent through it (see Fig. 239). Reactions (3) and (4) occur. It is essential to the success of this process, as was shown by the French metallurgist Manhès in 1880, that the air blast shall be admitted through ports in an annular pipe *above* the base of the converter, so that the metal formed drops below and is removed from the oxidising action of the blast; in steel-making, on the other hand, the blast is sent through the base of the converter.

Attempts have been made to smelt sulphide ores directly in a blast furnace, using the sulphur in the ore to supply most of the heat, but this method is not suitable for powdered ore and in America (*e.g.* at Anaconda) very large reverberatory furnaces with sand hearths and fired by gas, oil or powdered coal are used.

In copper extraction by *wet processes*, burnt pyrites are roasted with common salt to form cupric chloride which is dissolved in water. Any silver and gold present are precipitated as iodides by adding sodium

iodide, and the copper is then precipitated by scrap iron. Spanish Rio Tinto pyrites are stacked in immense heaps exposed to air and rain, when copper sulphate solution is formed and drains out; the copper is precipitated by scrap iron and the pyrites exported for sulphuric acid manufacture.

Copper refining.—The crude copper obtained by smelting is usually full of bubbles caused by the escape of gas in reaction (4) and is called *blister copper*. It may contain over 98 per cent. of copper but requires refining, for two reasons: (1) copper is used in making wires or cables for carrying electric current and the conductivity is appreciably lowered by traces of impurities; (2) the crude copper may contain traces of silver and gold, which pay for extraction.

The copper is often given a preliminary purification by melting on a furnace hearth, when atmospheric oxygen dissolves in the metal and oxidises impurities such as iron, which form a slag with silica. The small amount of cuprous oxide formed is removed by "poling", in which a pole of green wood is thrust into the melted metal. Torrents of reducing gas (containing methane) bubble up through the metal and reduce the oxide.

The blocks of copper are then finally purified by an electrolytic process. They are made the anodes in a bath of copper sulphate solution acidified with sulphuric acid. The cathodes are thin sheets of pure copper (Fig. 148). The copper dissolves from the anode as cupric ions Cu^{++} ;

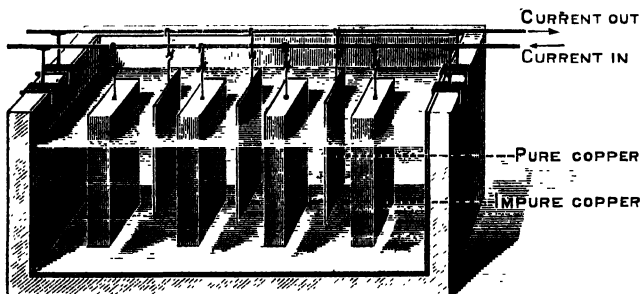


FIG. 148.—Purification of copper by electrolysis (diagrammatic).

these travel to the cathode, where they give up their charges and are deposited as pure copper. Iron, nickel, cobalt, arsenic and zinc pass into solution; gold, silver and any platinum metals (with some impurities, e.g. selenium, tellurium and lead) fall as an *anode slime*, which is collected for the purpose of obtaining the precious metals. The electrolytic copper is 99.96-99.99 per cent. pure.

The process of **electrotyping**, invented independently by T. Spencer and by Jacobi in 1837, is used for reproduction. The copper may be deposited on plaster casts covered with graphite to render them conducting, and the shell

stripped off. In the same way, if an impression of printers' type is taken on plastic material and the latter covered with powdered graphite, a thin deposit of copper may be formed over the surface by electrolysis. This is stripped off and backed by pouring on molten type-metal. The plate may then be used for printing.

Alloys of copper.—The alloys of copper with other metals are of technical importance. *Brass*, *Dutch metal*, *Muntz metal*, and *Delta metal* (copper + zinc), and *bronze*, *speculum metal* and *bell metal* (copper + tin), are made by fusing the copper, and adding the requisite amount of zinc or tin. *Coinage metal* contains copper, tin and zinc.

Ordinary bronze contains 9 of copper and 1 of tin. *Phosphor-bronze* contains 1 to 2 per cent. of phosphorus. *Silicon bronze* is used for telegraph wires. *Muntz metal* is used as a sheathing for wooden ships.

Properties of copper.—A new surface of pure copper appears salmon-pink in colour, but the colour produced by selective reflection is a deep rose-red, as is seen by looking at the fold of a piece of copper foil cleaned with nitric acid and bent to a V-shape. The light is then reflected many times from the surface of the metal before entering the eye. The complementary colour green is seen in the light transmitted through thin leaves of the metal. Fused copper also emits a green light at high temperatures.

Pure copper is very malleable and ductile and can be rolled into sheets, hammered into thin leaves, and drawn into wire. The metal may also be "spun" on the lathe in the production of seamless vessels. Just below the melting point copper becomes brittle, and small quantities of impurities reduce the malleability of the metal.

Pure copper powder is produced by dissolving zinc in a slightly acidified solution of copper sulphate, washing the precipitated copper with hot water and alcohol, and removing the small quantity of occluded hydrogen by heating in a vacuum.

Copper combines directly with chlorine, bromine, iodine, oxygen and sulphur.

In pure dry air copper remains bright, but in town air it rapidly tarnishes, becoming covered with a very thin adherent brown film. On prolonged exposure a green film of basic sulphate (see p. 314) is formed. On heating in air the metal is readily oxidised and the product forms scales which are black on the outside (cupric oxide CuO), but red on the side in contact with the metal (cuprous oxide Cu_2O). If heated for a long time in air cupric oxide is formed. When heated in the oxygen-hydrogen blowpipe the metal burns with a very brilliant green flame.

Copper does not decompose water at the ordinary temperature, or steam at a red heat.

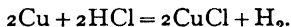
Copper is not acted upon by dilute sulphuric or hydrochloric acid in absence of oxygen; hot concentrated sulphuric acid converts it into the sulphate. The metal readily dissolves in dilute nitric acid (unless it is quite free from nitrous acid) with evolution of nitric oxide; it dissolves *with evolution of hydrogen* in hot concentrated hydrochloric acid, and more easily in hot concentrated hydrobromic and hydriodic acids.

Copper forms two series of compounds, the **cupric compounds** CuX_2 in which it is bivalent, and the **cuprous compounds** CuX in which it is univalent.

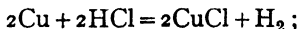
CUPROUS COMPOUNDS

Cuprous hydride CuH is obtained as an unstable brownish-yellow precipitate by reducing a solution of copper sulphate, acidified with a little sulphuric acid, with sodium hypophosphite at 70° . It evolves hydrogen with concentrated hydrochloric acid.

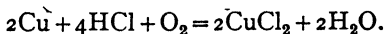
Cuprous chloride CuCl is formed as a brown mass when copper burns in a limited supply of chlorine, or hydrogen chloride is passed over heated copper :



Copper dissolves slowly in hot concentrated hydrochloric acid :

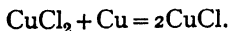


it dissolves more easily in presence of oxygen, when **cupric** chloride is first formed, but is reduced to CuCl by the copper :



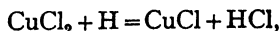
Cuprous chloride is most easily prepared by dissolving cuprous oxide in concentrated hydrochloric acid, or by reducing a solution of cupric chloride.

The cupric chloride may be reduced : (a) by boiling with concentrated hydrochloric acid and copper turnings until the solution becomes colourless :

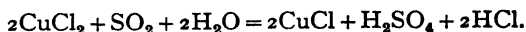


On pouring into water, white cuprous chloride is precipitated.

(b) By treating with zinc-dust and hydrochloric acid :



(c) by passing sulphur dioxide into the solution :



A mixture of cupric sulphate and sodium chloride may be used in the last case instead of cupric chloride.

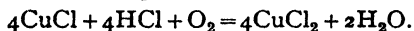
The following are convenient methods for the preparation of cuprous chloride :

A. Dissolve 25 gm. of cupric oxide in 250 c.c. of concentrated hydrochloric acid in a flask. Add 50 gm. of copper turnings and boil in a fume-cupboard until the solution is colourless. Pour into a litre of previously boiled distilled water, filter off the cuprous chloride in a Buchner funnel, and wash rapidly in succession with a dilute solution of sulphurous acid, alcohol, and ether. Dry in a vacuum desiccator on a porous plate over sulphuric acid.

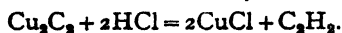
B. Pass sulphur dioxide into a solution of 25 gm. of crystallised copper sulphate and 12 gm. of common salt in 70 c.c. of water till the liquid, even on standing, smells strongly of the gas. Cuprous chloride slowly crystallises out and a further quantity separates after boiling ; it is filtered and treated as in *A.*

Cuprous chloride is a white powder which crystallises from concentrated hydrochloric acid in white tetrahedra. It melts on heating, forming a brown resinous mass on cooling. If exposed to light when moist it becomes dark coloured (*cf.* AgCl) ; in moist air it forms green *cupric* oxychloride $\text{CuCl}_2 \cdot \text{Cu}(\text{OH})_2$.

Cuprous chloride is insoluble in water but dissolves in *concentrated* hydrochloric acid to form a solution which is colourless when every trace of oxygen is excluded, *e.g.* by keeping in a closed bottle over bright copper turnings. The solution in hydrochloric acid, which probably contains the complex acid H_2CuCl_3 or the ion CuCl_3^- (containing 1-valent copper), rapidly becomes green or yellow on exposure to air owing to oxidation and formation of cupric chloride :

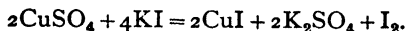


Cuprous chloride is soluble in sodium thiosulphate solution, and slightly soluble in potassium hydroxide solution. The solution in hydrochloric acid is used in gas analysis for the absorption of carbon monoxide, when a compound $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ is formed. Cuprous chloride dissolves readily in ammonia, forming a colourless solution of the cuprous ammine $\text{Cu}(\text{NH}_3)\text{Cl} \cdot \text{H}_2\text{O}$ if all traces of oxygen are excluded, as by standing over bright copper turnings in a closed bottle. Crystals of this compound are obtained by boiling copper powder with a solution of ammonium chloride, and cooling. The solution of cuprous chloride in ammonia becomes deep blue when exposed to air, the cupric ammine $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ (containing 2-valent copper) being formed. The ammoniacal solution of cuprous chloride is used in gas analysis to absorb carbon monoxide and acetylene ; with acetylene it forms a bright-red precipitate of *cuprous acetylide* Cu_2C_2 . This is explosive when dry ; when warmed with concentrated hydrochloric acid it evolves acetylene :

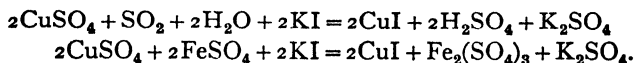


Cuprous bromide CuBr is a brown solid formed when bromine acts upon heated copper.

Cuprous iodide CuI is precipitated as a very insoluble white powder on addition of potassium iodide to a solution of cupric sulphate. Cupric iodide first produced is unstable and decomposes into cuprous iodide and free iodine :



If sulphur dioxide or ferrous sulphate is previously added, the iodine is reduced and forms cuprous iodide :



Dissolve 10 gm. of blue vitriol and 12.5 gm. of green vitriol in 250 c.c. of water and add 7.0 gm. of KI in 75 c.c. of water. Filter, wash, and dry the 7.5 gm. of CuI produced.

The formation of iodine in the first reaction is applied in the volumetric determination of copper.

Excess of potassium iodide solution is added, and not more than 3 c.c. of concentrated HCl or H_2SO_4 or (best) 25 c.c. of 50 per cent. acetic acid for 100 c.c. of solution. Starch is added when the yellow colour of the iodine is nearly discharged by thiosulphate and titration is continued till the colour is discharged. "After blueing" may occur on standing but is prevented by adding KCNS at the end of the titration. The solution should contain about 0.1 gm. of copper in the volume titrated and 5 times as much KI as copper is added.

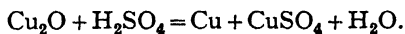
Cuprous oxide Cu_2O is a red solid formed by heating cupric oxide with copper or by the partial reduction of cupric compounds in the presence of alkalis, *e.g.* by boiling a solution containing cupric sulphate, sodium carbonate and sodium sulphite :



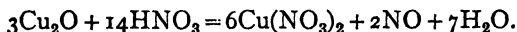
or by boiling a solution (Fehling's solution) containing cupric sulphate, Rochelle salt and sodium hydroxide, with grape sugar.

Dissolve 6.9 gm. of pure copper sulphate crystals in 100 c.c. of water, adding 1 drop of sulphuric acid. Call this *Solution A*. Dissolve in 100 c.c. of water 35 gm. of Rochelle salt (sodium potassium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) and 10 gm. of sodium hydroxide. Call this *Solution B*. Mix together 25 c.c. of *A* and 25 c.c. of *B* : the resulting deep-blue liquid is called *Fehling's solution*. Boil this in a porcelain dish with a solution of glucose (grape sugar). A yellow precipitate is deposited, which quickly turns to bright-red cuprous oxide Cu_2O . Filter, wash with boiling water and alcohol, and dry in a steam-oven.

Cuprous oxide gives a red colour to the borax bead. When fused with glass it forms the cheaper kind of *ruby glass*. With dilute sulphuric acid it gives a solution of *cupric* sulphate and metallic copper separates :

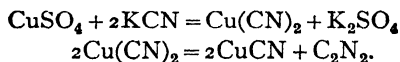


Dilute nitric acid dissolves cuprous oxide with evolution of oxides of nitrogen and a solution of *cupric* nitrate is formed :

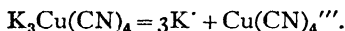


Concentrated hydrochloric acid dissolves cuprous oxide with formation of a colourless solution of *cuprous* chloride CuCl or a complex acid H_2CuCl_3 .

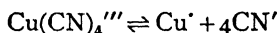
When potassium cyanide solution is added to a solution of cupric sulphate, the yellow cupric cyanide first precipitated rapidly decomposes with evolution of cyanogen gas and white *cuprous cyanide* CuCN is formed :



This dissolves in a solution of potassium cyanide, forming a colourless solution of *potassium cuprocyanide* $\text{K}_3\text{Cu}(\text{CN})_4$, which is a salt of a complex anion :

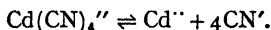


Only traces of copper ions are formed from the further ionisation :

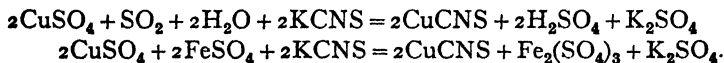


and the solution is not precipitated by hydrogen sulphide, since the concentration of copper ions is not sufficient to exceed the solubility product of the very sparingly soluble cuprous sulphide.

If cadmium is present, a complex cadmicyanide (p. 356) is formed, but the ion $\text{Cd}(\text{CN})_4''$ is sufficiently ionised to give enough cadmium ions to exceed the solubility product of cadmium sulphide :

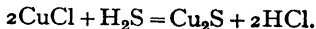


Potassium thiocyanate gives with a solution of cupric sulphate to which sulphur dioxide or ferrous sulphate has been added a white precipitate of *cuprous thiocyanate* CuCNS insoluble in hydrochloric acid :

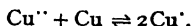


Cuprous sulphide Cu_2S , the stable sulphide of copper (p. 315), is formed as a blue-black brittle mass when sulphur and copper turnings are heated in a small flask, the copper burning in the sulphur vapour. The *pure* compound is obtained only when the reaction is carried out in a vacuum

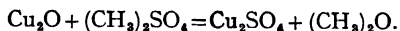
at a high temperature. Cuprous sulphide is also precipitated by hydrogen sulphide from a solution of cuprous chloride in hydrochloric acid :



Cuprous sulphate Cu_2SO_4 is formed to some extent when cupric sulphate solution stands in contact with copper :



This is the cause of the inaccuracy of the ordinary copper coulometer. The pure salt is obtained as a white powder by heating cuprous oxide with dimethyl sulphate, washing with ether and drying *in vacuo* :



It is at once decomposed by water, with deposition of copper : $\text{Cu}_2\text{SO}_4 = \text{CuSO}_4 + \text{Cu}$.

CUPRIC COMPOUNDS

Cupric chloride CuCl_2 is obtained anhydrous as a dark-brown mass by burning copper in excess of chlorine or by heating the hydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in hydrogen chloride gas at 150° . It is formed as a yellow powder by adding concentrated sulphuric acid slowly to a concentrated solution of cupric chloride. When strongly heated it loses chlorine and leaves cuprous chloride. A crystalline hydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is formed in emerald-green crystals by dissolving cupric oxide in concentrated hydrochloric acid and evaporating. When free from moisture the crystals are blue.

In concentrated solutions cupric chloride is yellowish-green ; on adding concentrated hydrochloric acid the colour becomes yellow. This is due to the reversal of the ionisation :



the colour of the undissociated salt (or perhaps a complex acid H_2CuCl_4) being yellow. A very dilute solution shows the pure blue colour of the hydrated cupric ion ; the green solutions probably contain a mixture of the blue ion and the yellow un-ionised form (or complex acid). Cupric chloride is very deliquescent and is also soluble in alcohol. The alcoholic solution burns with a fine green flame.

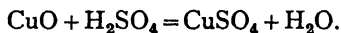
Cupric oxychloride $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ is formed as a pale-blue precipitate when caustic potash is added to an excess of cupric chloride solution. It occurs in Atacama, Peru, Bolivia, etc., in the form of a crystalline green sand called *atacamite*, and is being formed by the action of sea water on copper pyrites on the south coast of Chile. The oxychloride is prepared for use as a pigment called *Brunswick green* by boiling copper sulphate solution with a small quantity of bleaching powder.

Cupric bromide CuBr_2 is formed in black crystals by evaporating a solution of the oxide in hydrobromic acid in a vacuum desiccator over quicklime. In solution, it shows the same colour changes as the chloride.

Cupric iodide CuI_2 is so unstable that it at once decomposes into cuprous iodide and iodine, but in combination with ethylene diamine it is stable : $\text{CuI}_2 \cdot en_2$. Cupric nitrite, cyanide and sulphite behave similarly. The black cupric thiocyanate $\text{Cu}(\text{CNS})_2$, however, can be prepared as a solid.

Cupric oxide or *black oxide of copper* CuO is formed by prolonged heating of the metal (*e.g.* pieces of wire or turnings) in air or oxygen, or by heating cupric nitrate : $2\text{Cu}(\text{NO}_3)_2 = 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$. It is a black solid which is stable up to its melting point (about 1150°), but then evolves oxygen and leaves cuprous oxide Cu_2O and copper. Hot cupric oxide is readily reduced to metal by hydrogen, carbon or organic substances. The oxide dissolves in a borax bead, colouring it blue. If a little tin oxide or stannous chloride is added, the cupric oxide is reduced to cuprous oxide which forms an opaque red bead. Cupric oxide is used to give blue and green colours to glass.

When cupric oxide is dissolved in dilute acids, blue solutions of cupric salts are formed, *e.g.* :



Concentrated hydrochloric acid gives a yellow solution of cupric chloride CuCl_2 .

On adding a solution of alkali hydroxide to a solution of a cupric salt, a pale-blue gelatinous precipitate of cupric hydroxide is formed, insoluble in excess of alkali but soluble in ammonia. Unless excess of alkali is used, the precipitate (as stated by Berthollet) is a basic salt $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$, or $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$. If a little of the copper solution is added to an excess of concentrated alkali, a deep-blue colloidal solution is formed.

A crystalline hydroxide, $\text{Cu}(\text{OH})_2$, is obtained by adding ammonia to a boiling solution of copper sulphate till the green precipitate becomes blue, washing, and warming with fairly concentrated sodium hydroxide solution.

If the pale-blue precipitated hydroxide is boiled with water it forms a black solid usually formulated as $4\text{CuO} \cdot \text{H}_2\text{O}$ which is granular and easily filtered. On heating to dull redness this is converted into the oxide CuO .

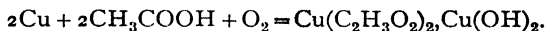
Only *basic cupric carbonates* are known ; the most important are the minerals *chessylite* (or *azurite*) $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (deep blue) and *malachite* $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (bright green). On heating, basic copper carbonates lose water and carbon dioxide and leave black cupric oxide.

The green patina formed on copper exposed to air, usually de-

scribed as the basic carbonate, is nearly always the basic sulphate $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$, which occurs as the mineral *brochantite*, although occasionally the basic carbonate is present. In places near the sea or where salt spray is carried by the wind the basic chloride $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (*atacamite*) is formed. The definite compounds are formed only after a prolonged exposure of about 70 years.

A mixture of basic carbonates called *verditer* is precipitated by a solution of sodium carbonate from a solution of a cupric salt. Azurite dissolves in a hot solution of sodium bicarbonate and on boiling the solution deposits a green powder of malachite.

Cupric acetate $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ forms dark-green crystals; the **basic acetate** $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}(\text{OH})_2$ is the bright-green pigment *verdigris*, made by allowing plates of copper to stand with alternate layers of "marcs" (grape skins after pressing the juice from the grapes in wine factories), then packing the sheets on end and moistening with sour wine, which forms acetic acid CH_3COOH :



Cupric nitrate is prepared by dissolving the metal, oxide or carbonate in dilute nitric acid, and on evaporation forms blue deliquescent prismatic crystals of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. On heating, the salt loses water and also nitric acid, forming a basic salt $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ which is also precipitated from solution by ammonia. Cupric nitrate decomposes on heating:



It possesses powerful oxidising properties: if a few crystals are moistened and wrapped in tinfoil, sparks are emitted. The anhydrous salt is obtained as a white powder by the action of a solution of nitrogen pentoxide in nitric acid on the crystalline hydrate.

Cupric sulphide CuS is a black solid formed by heating copper powder with excess of flowers of sulphur at a temperature below 440° ; by the action of a solution of sulphur in carbon disulphide on copper powder; or by precipitating an acid solution of a cupric salt with hydrogen sulphide. (The precipitate usually contains cuprous sulphide and sulphur.) In the moist state it is rapidly oxidised by air, forming a blue solution of the sulphate. It is slightly soluble in yellow ammonium sulphide. Cupric sulphide is less stable than cuprous sulphide and loses sulphur when gently heated alone or in hydrogen:



The commonest cupric salt is **cupric sulphate** CuSO_4 , commonly known simply as *copper sulphate*. This crystallises from water in large blue triclinic crystals $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ called *blue vitriol* or *bluestone*. It is obtained by dissolving cupric oxide or basic carbonate in dilute sulphuric

acid and crystallising. Anhydrous cupric sulphate is formed in the preparation of sulphur dioxide by heating copper with concentrated sulphuric acid :



Crystallised copper sulphate is obtained from the cold residue by dissolving in water, filtering and evaporating. Some black sulphide is also formed.

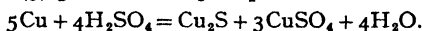
According to Cundall, the reaction leads first to the formation of cuprous sulphate Cu_2SO_4 ; if the acid liquid is cooled, filtered through asbestos, and poured into water, a red precipitate of copper is formed :



Cuprous sulphide Cu_2S deposits as a black powder in the earlier stages of the reaction, *but is afterwards mostly decomposed*.

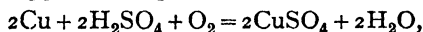
1. $8\text{Cu} + 4\text{H}_2\text{SO}_4 = 3\text{Cu}_2\text{SO}_4 + \text{Cu}_2\text{S} + 4\text{H}_2\text{O}.$
2. $2\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{Cu}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{SO}_2.$
3. $5\text{Cu}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4 = \text{Cu}_2\text{S} + 8\text{CuSO}_4 + 4\text{H}_2\text{O}.$
4. $\text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 = \text{CuS} + \text{CuSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2.$
5. $\text{CuS} + 4\text{H}_2\text{SO}_4 = \text{CuSO}_4 + 4\text{SO}_2 + 4\text{H}_2\text{O}.$

Equations (1) and (3) give Pickering's equation :

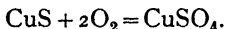


The final product is almost entirely CuSO_4 . Other sets of equations have been proposed.

Copper sulphate is prepared on the large scale by the action of dilute sulphuric acid on copper in the presence of air :



or by the "weathering" of copper pyrites, which may first be roasted :



Commercial cupric sulphate usually contains ferrous sulphate, with one hydrated form of which $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ it is isomorphous and forms mixed crystals. If the solution contains a considerable amount of copper, the crystals consist of $(\text{Cu}, \text{Fe})\text{SO}_4 \cdot 5\text{H}_2\text{O}$; if the iron predominates they have the composition $(\text{Fe}, \text{Cu})\text{SO}_4 \cdot 7\text{H}_2\text{O}$. Similar results are obtained with zinc sulphate.

Two basic sulphates, $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ and $\text{CuSO}_4 \cdot 4\text{Cu}(\text{OH})_2$ are formed by precipitating copper sulphate solution with suitable amounts of alkali hydroxide. Many double salts of copper sulphate, *e.g.* the light blue $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and the paler blue $(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, are formed by crystallising from solutions of the mixed salts.

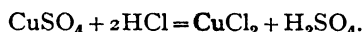
Copper sulphate is insoluble in alcohol and is precipitated in small crystals $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ when alcohol is added to the aqueous solution.

Several crystalline hydrates are known. On exposure to fairly dry air the blue pentahydrate crystals slowly effloresce to a pale-blue powder of $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. This (or the pentahydrate) at 100° forms a bluish-white powder of monohydrate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. At 260° this loses most of the combined water, but 0.04 per cent. is retained even at 360° , and the salt begins to lose sulphur trioxide at higher temperatures before all the water is expelled. Anhydrous copper sulphate is best prepared by heating the monohydrate for many hours at 240° in a current of dry air. The white powder obtained by dehydration at 260° is used in the detection of traces of moisture in alcohol, ether, etc., since it very readily absorbs water and becomes blue in colour.

Copper sulphate is stable up to 650° but at 750° it is completely decomposed, leaving a residue of cupric oxide :



Anhydrous or hydrated copper sulphate readily absorbs hydrogen chloride gas and is decomposed by the aqueous acid :



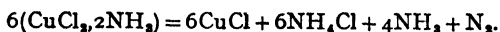
This reaction may be applied in separating hydrochloric acid from other gases, such as sulphur dioxide.

Copper sulphate is used in making green pigments, as a mordant in dyeing, and in making *Bordeaux mixture* (a mixture of the solution and milk of lime) as a wash to kill moulds and fungi on vines. The sulphate solution is also used in steeping wheat to prevent the growth of fungus.

Cupric hydroxide readily dissolves in ammonia, forming a deep-blue solution known as *Schweizer's reagent*. This dissolves cellulose (filter paper, cotton wool), and if the solution is squirted into dilute acid a thread of amorphous cellulose is formed which is one variety of artificial silk. The solution may also be applied to canvas to form a water-tight coating of amorphous cellulose (*Willesden canvas*). The blue ammoniacal solution contains the complex cation $\text{Cu}(\text{NH}_3)_4^{++}$, salts of which are known.

If a solution of cupric sulphate is precipitated with ammonia and the precipitate dissolved in excess of ammonia, a deep-blue solution is formed. If a layer of alcohol is poured carefully over this solution in a cylinder, the latter corked to prevent evaporation, and the whole allowed to stand, long transparent deep-blue rhombic prisms of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ are deposited. Cupric chloride forms $\text{Cu}(\text{NH}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ which crystallises on cooling a hot solution of cupric chloride saturated with ammonia gas. Anhydrous cupric sulphate absorbs ammonia gas, forming a blue powder of $\text{CuSO}_4 \cdot 5\text{NH}_3$, which dissociates to form $\text{CuSO}_4 \cdot 4\text{NH}_3$ and $\text{CuSO}_4 \cdot 2\text{NH}_3$. Anhydrous cupric chloride absorbs ammonia gas forming

$\text{CuCl}_2 \cdot 6\text{NH}_3$, which readily dissociates on heating, forming $\text{CuCl}_2 \cdot 4\text{NH}_3$, $3\text{CuCl}_2 \cdot 10\text{NH}_3$, and $\text{CuCl}_2 \cdot 2\text{NH}_3$. The latter on heating decomposes as follows :



The atomic weight of copper proved very difficult to find exactly. Richards determined the ratios $\text{CuBr}_2 : 2\text{AgBr}$, and $\text{Cu} : \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (which gave a poor result), etc., and also compared the weights of copper and silver deposited by electrolysis. The valency follows from the atomic heat.

SILVER

History.—Silver was known in Predynastic Egypt (c. 4000 B.C.) but was very rare. A fine Chaldean silver vase of 2850 B.C. is in the Louvre.

Occurrence.—Silver occurs in the native state, occasionally nearly pure but usually containing copper and gold. Important ores of silver are the sulphide *argentite* (or *silver glance*) Ag_2S (the commonest ore); *chlorargyrite* (or *horn-silver*) AgCl ; *pyrargyrite* (or *ruby-silver*) Ag_3SbS_3 ; *stromeyerite* (or *silver-copper glance*) $(\text{Cu}, \text{Ag})_2\text{S}$; and *stephanite* Ag_5SbS_4 . Less important are *proustite* Ag_3AsS_3 , *bromargyrite* AgBr , and *iodargyrite* AgI . Most copper and lead ores contain small amounts of silver, which is extracted in copper refining (p. 307) and from argentiferous lead; silver is extracted from the ores of the Ontario cobalt mines, and in North America, Mexico and Broken Hill (N.S. Wales).

Metallurgy.—Silver is extracted from its ores by several processes.

I. The **cupellation process** is the oldest. It is mentioned in the Bible and is described by Strabo and by Pliny as in use in Spain. Lead from galena is nearly always argentiferous and forms an important source of silver and the process is also used with alloys formed by smelting lead and silver ores together. The argentiferous lead is first “desilvered” by the Pattinson or Parkes process (see below) and the lead-silver alloy rich in silver is then melted on a flat dish or *cupel* formed of bone-ash. A blast of air is driven over the surface of the molten metal (Fig. 149) when the lead is oxidised to lead monoxide or litharge PbO , which fuses and is swept off by the air blast. The last portions of litharge are absorbed by the porous cupel and a bright mass of silver is left.

When the metal contains 60-70 per cent. Ag the temperature is raised and a little sodium nitrate added to remove impurities. In the last stage of the process the litharge film becomes so thin that iridescent colours are seen; the bright silver surface then “flashes” out (an appearance sometimes called by the German name “blick”) and the metal contains 99.5 per cent. of silver.

II. The Pattinson process (1833). On cooling fused argentiferous lead nearly pure lead separates. The crystals are removed by perforated iron ladles and the remaining liquid alloy becomes richer in silver. If the process were carried far enough, lead and silver would begin to separate out together at the eutectic point (2.5 per cent. Ag). In practice seven-eighths of the lead are removed. The process is carried out in a row of ten iron pots, the lead separated being passed on from pot to pot to be remelted and the liquid alloy passed in the other direction. The silver gradually accumulates in the alloy at one end of the series, and desilvered lead at the other. The rich alloy is then cupelled.

In the modification known as the **Luce-Rozan process** only two pots are used, a small upper melting pot and a large lower crystallising pot.

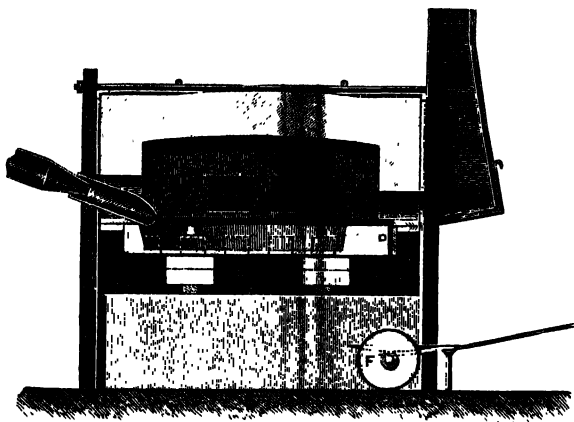


FIG. 149.—Cupellation furnace.

The lead is deposited in the latter by blowing steam at 50 lb. pressure through the fused metal, whilst cold water is sprayed on the surface. When two-thirds of the lead have separated the liquid is strained off through a perforated plate. The separated lead is remelted and the process repeated until the proportion of silver mechanically retained in the lead crystals is sufficiently small. In this process any copper and antimony are removed from the lead.

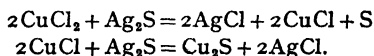
III. The Parkes process (1850). Molten lead dissolves only about 1 per cent. of zinc and molten zinc only 1 per cent. of lead. Silver, however, is soluble in zinc. One or two per cent. of zinc is added to fused argentiferous lead at a temperature above the melting point of zinc, when the molten alloy of zinc and silver floats to the surface and solidifies on cooling. A second lot of zinc is then added. The crust is skimmed off with a perforated ladle and strongly heated with carbon in a fire-clay retort. Zinc distils leaving silver which is cupelled. A continuous process is also used. The Parkes is superseding the Pattinson process.

The zinc alloy may also be electrolysed (as anode) in zinc chloride solution; zinc is deposited on the cathode and silver is left. To remove traces of zinc dissolved in the lead, the latter is heated to redness and a blast of steam forced through it, when zinc oxide rises to the surface. Zinc is now often removed as chloride by treatment with chlorine.

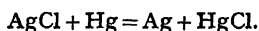
Any gold and copper present are also removed by the zinc. The desilvered lead contains only 0.0004 per cent. of silver, whilst that obtained by the Pattinson process contains 0.001-0.002 per cent. If bismuth is present (which may be objectionable and is difficult to remove from the lead), it goes to the argentiferous part in the Pattinson process, but remains in the lead in the Parkes process.

IV. Amalgamation process. The amalgamation process has been used since the sixteenth century in Mexico, where fuel is scarce, but is being replaced by the cyanide process (see below).

The ores containing metallic silver, silver chloride and sulphide and a large quantity of rock are finely crushed in stamping mills worked by mules, and the fine mud mixed with a little salt is then well trodden by mules on a paved floor or *patio*. Mercury is then added together with a little roasted pyrites, containing cupric and ferric sulphates, and the treading is continued for fifteen to forty-five days. Copper chlorides are probably first produced from the roasted pyrites and salt, and these decompose the silver sulphide with formation of the chloride:

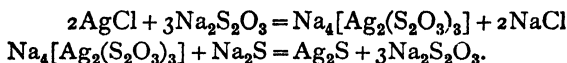


The silver chloride then dissolves in the salt brine and is reduced by the finely divided mercury:

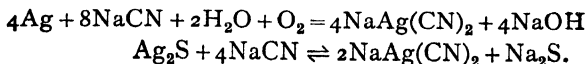


The silver amalgamates with the excess of mercury. The amalgam is separated by washing, the excess of mercury is pressed out in canvas bags, and the residue is distilled in iron retorts to recover the mercury.

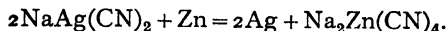
V. Wet processes (Percy and Patera, Augustin, Ziervogel, etc.). The ore is roasted either alone when soluble silver sulphate is formed and can be lixiviated, or with salt when silver chloride is produced which is extracted with hot common salt solution or a solution of sodium thio-sulphate. From these solutions the silver is precipitated by sodium sulphide as silver sulphide:



In the modern cyanide process the unroasted ore or concentrate, finely ground in ball mills, is leached with a dilute solution of sodium cyanide, the slime being well agitated by a stream of air. Soluble sodium argentocyanide $\text{NaAg}(\text{CN})_2$ is formed:



The sodium sulphide is oxidised to sulphate by the aeration. The silver is precipitated from the solution by zinc :



Silver is now largely obtained from native silver in Mexico, the U.S.A., and Canada. Some comes from gold and copper refining, and from ores of other metals (copper, zinc, and lead).

Silver is *refined* by cupellation or by electrolysis in silver nitrate solution with about 1 per cent. of free nitric acid ; the cathode is a plate of pure silver and the anode a block of the silver to be refined. Silver is deposited, copper dissolves, and the gold present in the anode deposits as a slime which is collected in a canvas bag.

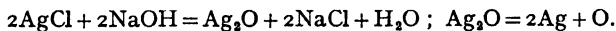
Pure silver.—In order to obtain pure silver, its commercial alloy with copper is dissolved in dilute nitric acid, when copper and silver nitrates are formed. The solution is evaporated and diluted with water. Hydrochloric acid is added to precipitate silver chloride. This is filtered off and washed with hot water till free from acid. Silver chloride is also formed by adding hydrochloric acid to laboratory "silver residues". Silver can be obtained from the chloride in several ways.

(a) The dry chloride is fused in a crucible with sodium carbonate, when a button of pure silver is formed :



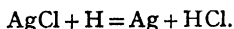
A crucible furnace should be used, as silver has rather a high melting point (960°).

(b) The moist silver chloride is boiled with caustic soda solution and grape sugar : the oxide first formed is converted into a grey powder of metallic silver, together with a dark-brown solution containing the oxidation products of the sugar :



The silver is then well washed with boiling distilled water.

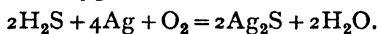
(c) Dilute sulphuric acid is poured over the moist silver chloride and a stick of pure zinc placed in the mixture. The chloride is reduced, forming a grey mass of silver powder (*molecular silver*), which is washed and dried :



The silver from (b) or (c) may be fused in a crucible with sodium carbonate to form a button. (If silver is fused in a glazed porcelain crucible, the latter becomes yellow, owing to the formation of silver silicate). Richards showed that pure fused silver contains a little occluded oxygen, which may be removed by fusion on lime in an atmosphere of hydrogen.

Properties of silver.—Silver is a pure white metal, which conducts heat and electricity better than any other metal. It boils at a very high temperature forming a blue vapour, the density corresponding with the formula Ag . Silver is very malleable and ductile ; it can be beaten into leaves, which become somewhat transparent on heating. Very thin films deposited on glass transmit blue light.

Silver, like gold and platinum, is a “noble” metal, *i.e.* it is not oxidised in air either in the cold or when heated. On exposure to ordinary air it slowly tarnishes and becomes covered with an adherent film, which is yellow, blue and black with increasing thickness. This film is composed of silver sulphide Ag_2S , formed by the decomposition of hydrogen sulphide in the air in presence of oxygen :



The staining of silver spoons used with eggs is also due to the formation of silver sulphide from the combined sulphur in the albumin of the egg. The tarnish is readily removed by a dilute solution of potassium cyanide (*poisonous!*), followed by washing in plenty of water.

Fused silver dissolves up to 20 times its volume of oxygen which is liberated as soon as the metal begins to solidify, when the metal “spits”, part of the fused metal being forced out as globules or excrescences. This is a good test of the completion of cupellation. It is prevented by covering the metal with charcoal powder. Silver is attacked by chlorine, and more slowly by bromine, iodine and sulphur. It dissolves in concentrated hydriodic acid with evolution of hydrogen. It is not attacked by hydrochloric acid or dilute sulphuric acid, but is attacked by boiling concentrated sulphuric acid or cold dilute nitric acid. Silver resists the action of alkalis, even fused, hence silver crucibles are used for fusion with caustic alkalis, but may be replaced by those of pure nickel, although the latter is slightly attacked.

Silver deposited on glass by reduction is used in the manufacture of mirrors. This may be demonstrated as follows.

Clean a test-tube with boiling nitric acid, wash well with water, and prepare in it a dilute solution of silver nitrate. Add *dilute ammonia* drop by drop until the brown precipitate of silver oxide is *almost* redissolved. Then add caustic potash and a solution of Rochelle salt or grape sugar, which acts as the reducing agent. Place the tube in a beaker of hot water. A mirror of silver is deposited on the tube.

A *colloidal solution* of silver may be prepared by Bredig’s method of striking an electric arc between silver wires under water. The metal is volatilised, and condensed in the water in the form of very small particles which remain in colloidal suspension. Colloidal silver is also formed by

reduction with ferrous sulphate, etc., in presence of sodium citrate, when a red transparent solution is formed. Colloidal silver stabilised by alkaline albumin solution is called *protargol* and is a dark-brown liquid used as a disinfectant in ophthalmic cases.

Commercial silver is alloyed with copper because the pure metal is too soft for coinage or jewellery work. The proportion of silver in 1000 parts of alloy is called the *fineness*.

Electroplating with silver.—The electrodeposition of silver is applied in the silver coulometer (p. 195).

This (Fig. 150) consists of a platinum crucible, which is carefully weighed and contains a 30 per cent. solution of silver nitrate. The crucible is placed on a brass plate, which is the negative terminal. The anode is a rod of pure silver suspended in the solution. A small glass cup is suspended under the anode to retain detached pieces. The crystalline deposit of silver is washed with water and alcohol, and the crucible is dried in an air-oven and weighed.

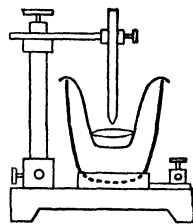
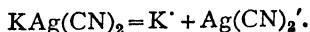
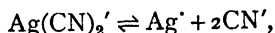


FIG. 150.—Silver coulometer.

Copper articles are electroplated with silver by making them the cathode in a solution of silver cyanide in excess of potassium cyanide, the anode being a plate of pure silver. The solution contains **potassium argentocyanide** :



The anion is very slightly dissociated :



and the silver ions are deposited on the cathode as a coherent film of metal instead of the crystalline metal formed from silver nitrate solution. The cyanide ions discharged on the silver anode form silver cyanide, which dissolves in the solution. The net result is the transfer of silver from the anode to the cathode.

Formerly, copper goods were plated by laying a strip of silver on a bar of clean copper, heating, and rolling the bar to the required thickness. This is known as *Sheffield plate*, and the layer of silver is much thicker than with electroplated goods.

SILVER COMPOUNDS

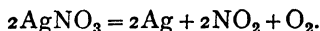
Silver in its ordinary compounds is univalent, but a few compounds of bivalent silver are known. Silver does not form basic salts, thus differing from copper. The silver salts are largely ionised in solu-

a white double carbonate AgKCO_3 is precipitated. Moist silver oxide absorbs carbon dioxide to form silver carbonate.

Silver acetylide Ag_2C_2 is an explosive white solid precipitated by acetylene from ammoniacal silver nitrate solution.

Silver nitrate AgNO_3 is the most important silver salt. It is made by dissolving silver in hot dilute nitric acid, evaporating and crystallising, when colourless transparent rhombic crystals are formed, which are very soluble in water. It is also soluble in alcohol. The salt readily fuses and when cast into sticks forms *lunar caustic*. Silver nitrate is readily decomposed by organic matter such as paper, cork or the skin, deep-black metallic silver being deposited, so that a solution of silver nitrate is used as an indelible ink for marking linen. The black stain can be removed from the articles by a dilute solution of potassium cyanide.

Silver nitrate decomposes when strongly heated, when oxygen and nitrogen dioxide are evolved and silver remains :



The decomposition point is much higher than that of copper nitrate, so that this may be separated from silver nitrate by heating, adding water, and filtering from the copper oxide.

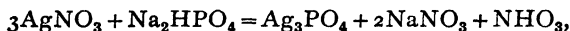
Solid silver nitrate absorbs ammonia gas with evolution of heat and forms a compound $\text{AgNO}_3 \cdot 3\text{NH}_3$. If ammonia is added to a solution of the nitrate until the oxide first precipitated is dissolved, and the liquid is evaporated out of contact with air, crystals of a compound $\text{AgNO}_3 \cdot 2\text{NH}_3$ separate. Double salts, e.g. $\text{AgNO}_3 \cdot \text{NH}_4\text{NO}_3$ and $\text{AgNO}_3 \cdot \text{KNO}_3$, are known.

Silver nitrite AgNO_2 is formed as a yellowish-white precipitate when solutions of silver nitrate and sodium nitrite are mixed. It may be crystallised from hot water. It decomposes on heating, evolving nitric oxide and leaving silver nitrate and silver :

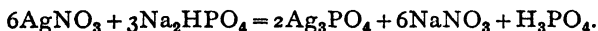


Silver phosphide Ag_3P_2 is formed from the elements on heating.

Silver orthophosphate Ag_3PO_4 is formed as a pale-yellow precipitate when a solution of sodium phosphate is added to one of silver nitrate. The reaction is usually represented by the equation :



but as the precipitate is readily soluble in nitric acid, only about two-thirds of this amount of silver is precipitated :



The **acid phosphate** Ag_2HPO_4 is deposited in white crystals from a solution of the phosphate in phosphoric acid. The **metaphosphate** AgPO_3 and

pyrophosphate $\text{Ag}_4\text{P}_2\text{O}_7$ are white precipitates formed by adding silver nitrate to the corresponding sodium salts. Silver arsenite Ag_3AsO_3 and silver arsenate Ag_3AsO_4 are canary-yellow and light chocolate-brown precipitates, respectively. The arsenite dissolves in ammonia, and if the solution is boiled silver is deposited :



Silver sulphide Ag_2S is a black solid formed when silver is heated with sulphur or in hydrogen sulphide, or silver nitrate is precipitated with the latter.

Silver sulphate Ag_2SO_4 is formed by boiling silver with concentrated sulphuric acid, or by precipitating a solution of the nitrate with a sulphate. It is sparingly soluble in water, but dissolves readily in dilute or concentrated sulphuric acid, or in dilute nitric acid. Silver sulphate decomposes at a red heat :



The acid sulphate AgHSO_4 is formed in light-yellow crystals when the sulphate is dissolved in less than three parts of sulphuric acid.

Photography.—The blackening of silver chloride on exposure to light is mentioned by Boyle ; Scheele in 1777 proved that metallic silver is formed. The development of this discovery into photography took place early in the nineteenth century. Recent experiments with the micro-balance have proved that silver chloride is decomposed by light into chlorine and metallic silver, not a subhalide.

In the modern process the light-sensitive medium is a suspension or " emulsion " of silver halide particles in gelatin. High-speed plates and films contain a mixture of silver bromide with a little iodide ; process plates, fast lantern plates and bromide papers contain silver bromide ; warm-tone " chlorobromide " papers and lantern plates contain a mixture of chloride and bromide ; gaslight papers contain chloride.

On exposure in the camera, a " latent image " is formed, parts of the grains of silver halide exposed to light being converted into minute spots of metallic silver. On developing in a solution of a reducing agent, the whole affected grain is reduced to black silver, the minute spots of silver on the grain acting as nuclei. The unchanged silver halide is then removed by " fixing " in a solution of sodium thiosulphate, which dissolves it. A " positive " print is then made from this " negative " on paper faced with a silver halide emulsion. The print is " toned " by immersion in a solution containing gold (giving a brown to purple tone) or platinum (giving a grey tone)—the metal replacing some silver, which dissolves—and is then fixed in the same way as the negative. By adding certain dyes to the emulsion on the plate or film, increased sensitivity to longer wave-lengths is conferred and even infra-red photography is possible.

Bivalent silver. Apart from the oxide AgO and a stable bifluoride AgF_2 , no simple compounds of bivalent silver are known, but some dark

coloured complex compounds have been prepared containing pyridine (py), etc., which stabilise the bivalent silver, *e.g.* $[\text{Agpy}_4](\text{NO}_3)_2$, obtained by electrolytic oxidation.

The atomic weight of silver is discussed on p. 76.

GOLD

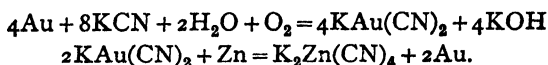
History.—Gold occurs in the free state and with its marked colour and brilliance was probably one of the first metals known to man. Gold ornaments are found in neolithic remains.

Occurrence.—Gold usually occurs native, alloyed with a certain amount of silver and sometimes copper and traces of platinum. Some tellurium compounds of gold occur in small amounts, and traces of gold are found in all igneous rocks, in pyrites and other ores, and in sea water (less than $\frac{1}{10}$ th grain per ton). Gold is recovered from burnt pyrites.

Electrum is a native alloy of gold and silver, containing 15 to 45 per cent. of silver; *green gold* contains 10 per cent. of silver. These alloys were used in ancient Egypt and called *asem*. Australian gold sometimes contains an appreciable amount of silver.

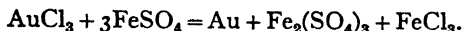
Metallurgy.—The gold sometimes occurs in isolated “nuggets” or grains in sands or alluvial gravels, or else in hard quartz “reefs”. The gravels are broken up by powerful jets of water, and the rock is crushed in stamping mills or usually in ball-mills. By modern processes, quartz containing only 0.001 per cent., and gravels containing only 0.00003 per cent., of gold can be profitably worked. From the gravel washing, grains of gold are separated by passing the mud through long wooden troughs with battens across the bottom or over blankets, which catch the heavier gold particles, the particles of rock being washed away. The slime from mills is sometimes passed over amalgamated copper plates, when the gold adheres to the mercury, but the **cyanide process** (MacArthur and Forrest, 1887) is now generally used and can be applied to finely stamped ore or “tailings” from other processes.

The material is percolated in large vats with false bottoms with a weak solution of potassium or sodium cyanide in which, when exposed to air, the gold dissolves. The solution containing the complex aurocyanide $\text{KAu}(\text{CN})_2$ is reduced by adding charcoal or passing through boxes containing thin zinc shavings (the packages in which the cyanide is exported supply the zinc), when gold is precipitated as a black mud. The powder is fused in graphite crucibles and sent for refining:



Auriferous pyrites or “concentrates” are treated by Plattner’s “chlorine process”; they are roasted, moistened with water and exposed to chlorine gas in tubs with false bottoms, when gold dissolves as tri-

chloride AuCl_3 . This is washed out with water and the solution reduced with charcoal or ferrous sulphate :



Bromine water is now often used instead of chlorine.

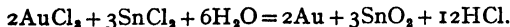
The gold bullion is *refined* in various ways. If it contains silver it may be boiled with nitric or concentrated sulphuric acid, which dissolve the silver, provided the alloy does not contain more than one-third its weight of gold ; if it contains more gold it is melted with silver to form an alloy which contains one-quarter its weight of gold, hence the process is called "quartation".

In the Miller process, used at the Ottawa Mint, chlorine gas is passed through the melted metal covered with borax, when silver chloride is formed and floats to the top. In an electrolytic process, the gold bullion is made the anode in gold chloride solution containing hydrochloric acid, pure gold being deposited on the cathode.

Properties.—Gold is a bright-yellow metal of high density and is a good conductor of heat and electricity. Its melting point (1063°) lies between those of silver (961°) and copper (1083°). Gold is the most ductile and malleable of all metals ; it can be beaten into leaves less than 0.0001 mm. thick by first beating between sheets of vellum and finally between sheets of gold-beater's skin. Gold leaf transmits green light, which is seen by holding burning magnesium behind gold leaf between two sheets of glass. Deposits on gold lace are only 0.000002 mm. thick but still show the metallic lustre.

Gold is not attacked by oxygen at any temperature nor by single acids except selenic and iodic. It dissolves in chlorine water or in *aqua regia* (a mixture of concentrated nitric and hydrochloric acids which liberates chlorine). It is attacked by fused alkalis (unlike silver) and by fused nitre. Gold compounds are very easily reduced to the metal.

Colloidal gold is formed by Bredig's process (p. 322) or by reducing a solution of gold chloride with phosphorus, ferrous sulphate, formaldehyde, etc. The solutions are ruby-red when the gold particles are very fine, and blue with coarser particles ; the red solutions are more stable in presence of a little gelatin. By precipitating gold chloride solution with stannous chloride, a purple powder called *purple of Cassius* (discovered by Andreas Cassius and described in 1684) is thrown down ; according to Moissan this is a colloidal form of stannic oxide with adsorbed colloidal gold :



It is used in making gold ruby glass ; the glass when fused with the powder is at first colourless, but the red colour develops on annealing.

Gold is too soft for use in the pure state, so that it is alloyed with copper or silver, or both. Copper makes the metal redder, silver makes it pale. These alloys are malleable. Traces of lead and bismuth make gold brittle ; a purple alloy containing AuAl_2 is formed with aluminium.

The "fineness" of a gold alloy is often expressed in "carats", pure gold being 24 carat fine and standard alloys are 22, 18, 15, 12 and 9 carat, containing these proportions of gold in 24 parts. The alloy is "assayed" by cupellation with lead, the button containing gold and silver being then "parted" by flattening, heating with nitric acid to dissolve the silver, heating to redness and weighing on an assay balance.

Gold plating is carried out in the same way as silver plating by deposition from a bath containing gold cyanide dissolved in potassium cyanide, the requisite amounts of copper and silver being added, when these metals are deposited with the gold.

Gold coinage has almost entirely gone out of use, the metal being stored in ingots in vaults as a standard of value. The great rise in price of gold has made it profitable to work deeper and poorer lodes than was formerly thought possible.

Compounds of gold.—Gold forms two series of compounds in which it is uni- and tervalent: AuX and AuX_3 . It unites directly with chlorine and bromine to form auric chloride AuCl_3 and auric bromide AuBr_3 . On careful heating, these evolve free halogen and form aurous chloride AuCl , and aurous bromide AuBr . At still higher temperatures, these lose halogen and form metallic gold. By dissolving gold in *aqua regia* and evaporating, deliquescent yellow crystals of chloroauric acid $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (commonly known as "gold chloride"), soluble in alcohol and ether, are formed. On heating, these form AuCl_3 ; with concentrated hydrochloric acid and potassium chloride the salt KAuCl_4 is formed. Auric oxide Au_2O_3 is formed on gently heating auric hydroxide $\text{Au}(\text{OH})_3$, precipitated from chloroauric acid solution by magnesia. Aurous iodide AuI is precipitated from auric chloride solution by potassium iodide (cf. copper).

CHAPTER XXIII

THE ALKALINE-EARTH METALS

THE elements of Group II in the Periodic Table are all metals. They are divided into two sub-groups, the odd series and the even series :

- (a) **Even series:** beryllium, magnesium, calcium, strontium, barium and radium. (b) **Odd series:** zinc, cadmium and mercury.

In many ways beryllium and magnesium resemble more closely the metals of the (b) series. Radium has been described in Chapter XX.

All these metals are bivalent in all their compounds. The so-called cadmous salts (Cd_2O , CdCl) are mixtures of bivalent cadmium compounds and finely divided metal. The mercurous salts such as calomel HgCl , in which the metal seems to be univalent, have the doubled formulae Hg_2X_2 , in which the group —Hg—Hg— , made up of two bivalent mercury atoms, is also bivalent. All these metals form stable basic oxides RO and (except mercury) hydroxides R(OH)_2 . There is a regular increase in the solubility of these hydroxides in series (a) with increase in atomic weight ; those of series (b) are practically insoluble in water.

The older chemists gave the name **earth** to all non-metallic substances insoluble in water and unchanged by fire. Lime and magnesia were found to have an alkaline reaction and were called **alkaline earths**, the name being afterwards applied to baryta (Scheele, 1774) and strontia (Hope, 1792). The metals themselves were isolated by Davy (1808) by the electrolysis of solutions of the chlorides with a mercury cathode, and distilling the amalgams so formed. Lavoisier had suggested that, like other "bases", the earths were oxides of metals. The metals were obtained in a coherent form by Bunsen and Matthiessen in 1855-6 by electrolysis of the fused chlorides with a carbon anode and a thin iron wire cathode.

The metals of the alkaline earths are all silver-white, oxidise in the air and decompose water, though less vigorously than the alkali metals. Magnesium, calcium, strontium and barium form hydrides MH_2 directly (magnesium under pressure) ; beryllium and the metals of the odd series also form hydrides but only indirectly. Calcium, strontium and barium form peroxides MO_2 from the monoxides and oxygen ; a magnesium peroxide is described (p. 334). The peroxides form hydrogen peroxide with acids and contain the group —O—O— combined with the bivalent

metal atom (p. 146). The metals of the even series combine directly with nitrogen, forming nitrides M_3N_2 . The compounds of some give distinctive colours when moistened with hydrochloric acid and heated on platinum wire in the bunsen flame : calcium, orange-red ; strontium, crimson ; barium, apple-green ; radium, carmine-red.

MAGNESIUM

History.—In 1695 Nehemiah Grew obtained from the water of a mineral spring at Epsom a peculiar salt which was called *Epsom salt*, which is **magnesium sulphate** $MgSO_4 \cdot 7H_2O$; **magnesium chloride** $MgCl_2$ is contained in sea water. By precipitating solutions of these salts with potassium or sodium carbonate, a basic carbonate called *magnesia alba* is obtained. Black in 1754 showed that this contains fixed air or carbon dioxide combined with *calcined magnesia* or **magnesium oxide** MgO , left after ignition of *magnesia alba*. Metallic magnesium was obtained in an impure state by Davy in 1808, and the coherent metal by Bussy in 1830 by fusing the anhydrous chloride with potassium.

Occurrence.—Magnesium is widely distributed, occurring as *magnesite* $MgCO_3$, *dolomite* $MgCO_3 \cdot CaCO_3$, *kieserite* $MgSO_4 \cdot H_2O$, *kainite* $MgSO_4 \cdot K_2SO_4 \cdot MgCl_2 \cdot 6H_2O$ and *carnallite* $KCl \cdot MgCl_2 \cdot 6H_2O$. It is also contained in *spinel* $MgAl_2O_4$ and *olivine* Mg_2SiO_4 ; *talç* and *meerschau* are hydrated silicates, *asbestos* is calcium magnesium silicate, and other common rock-forming minerals containing magnesium silicate are *augite* and *serpentine*. All plants and animal tissues contain small amounts of magnesium ; it is contained in *chlorophyll*, the green colouring-matter of plants.

Magnesium.—Metallic magnesium is prepared by the electrolysis of the fused magnesium chloride and potassium chloride obtained by heating carnallite. The cathode is the iron crucible, the anode is of carbon enclosed in a porcelain tube. The chlorine is led off and the metal floats to the surface, being protected by a current of hydrogen or coal gas. The electrolysis of magnesium oxide dissolved in molten magnesium fluoride is also used. The semi-fused metal is pressed into wire, which is then rolled into ribbon.

Magnesium is a brilliant white metal, which is stable in dry air but soon becomes covered with oxide in moist air. It burns with an intense white light when heated in air, producing the oxide MgO and a little nitride Mg_3N_2 . It also continues to burn in sulphur vapour, steam, carbon dioxide, sulphur dioxide, nitric oxide and nitrogen dioxide ; it reduces carbon monoxide when heated. Magnesium reduces sodium and potassium oxides on heating. Magnesium powder mixed with powdered potassium chlorate or barium peroxide burns explosively when kindled, producing a blinding white flash ; the mixture is used in

photography and for signalling and star-shells. A mixture of magnesium and dry amorphous silica may also be used.

Although the metal has a high boiling point, fine crystals are obtained by sublimation in a vacuum tube below 600° . It is a very light metal and is a constituent of light alloys. Magnesium is used as a "getter" in radio-valves to remove the last trace of gas from the bulb: the metal is put on the filament and volatilised by heat, condensing as a bright mirror on the glass. Phosphorus is also used as a "getter."

Magnesium dissolves readily in dilute acids, but not in alkalis. Magnesium powder decomposes hot water and the amalgam decomposes cold water.

MAGNESIUM COMPOUNDS

Magnesium fluoride MgF_2 is sparingly soluble and is precipitated by a solution of sodium fluoride from a solution of a magnesium salt.

Magnesium chloride MgCl_2 is very soluble. It is usually prepared from *carnallite* $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ which occurs in large quantities in the Stassfurt deposits. It fuses at 176° , undergoing decomposition with deposition of practically all the potassium chloride, and fused magnesium chloride $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ remains, which crystallises on cooling. The crystals are very deliquescent and are used in lubricating cotton thread in spinning. Magnesium chloride forms hydrates with 12, 8, 6, 4 and $2\text{H}_2\text{O}$. Magnesium salts are very little hydrolysed in solution, since magnesia is a strong base, but if the crystalline hydrates of magnesium chloride are heated they undergo hydrolysis; hydrochloric acid and steam are evolved and an **oxychloride** Mg_2OCl_2 is left, and on strongly heating in air this evolves *chlorine* and leaves the oxide. Anhydrous magnesium chloride is prepared by heating the hexahydrate in a vacuum or in a current of hydrogen chloride. Another method is to add ammonium chloride to the solution, evaporate, and heat. The double salt $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ which is left on evaporation loses water and the residual $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl}$ on further ignition evolves hydrogen chloride and ammonia, leaving fused anhydrous magnesium chloride.

If a concentrated solution of magnesium chloride is mixed with magnesium oxide, the paste solidifies to a hard white mass of a hydrated **oxychloride**, $\text{MgCl}_2 \cdot 5\text{MgO}$, used as a cement (*Sorel's cement*) and as a finish for plaster, since it takes a fine polish.

Magnesium bromide $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ and **iodide** $\text{MgI}_2 \cdot 8\text{H}_2\text{O}$ occur in some mineral springs and are prepared in the same way as the chloride, by dissolving magnesium oxide or carbonate in the acids.

Magnesium oxide MgO occurs in octahedral crystals as the mineral *periclase*. It is formed as a white powder by burning the metal in air or oxygen, and by heating the hydroxide, nitrate, basic carbonate or native carbonate (*magnesite*). When prepared by heating the carbonate, it is known as *calcined magnesia*. Two varieties are formed, light and heavy, from the corresponding carbonates. Magnesium oxide is only very sparingly soluble, but it slowly combines with water, forming the hydroxide, and it turns moist red litmus paper blue. It fuses only at a very high temperature and is used for refractory bricks for furnaces. It is reduced by carbon in the electric furnace, forming magnesium carbide. A crystalline oxide is produced by heating the powder strongly in a current of hydrogen chloride.

Magnesium hydroxide $\text{Mg}(\text{OH})_2$ occurs crystalline as the mineral *brucite*. It is prepared by precipitating a solution of magnesium sulphate or chloride with alkali hydroxide; the white precipitate (insoluble in excess of alkali) is washed and dried at 100° . On the large scale it is made by precipitating a solution of magnesium chloride with milk of lime.

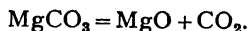
The solubility of magnesium hydroxide (0.01 gm. per litre of water) is reduced by addition of alkali hydroxide, but increased by addition of ammonia and especially of ammonium chloride. This reaction is applied in qualitative analysis, where magnesium is kept in solution by ammonium chloride whilst the metals of the groups III, IV, and V are precipitated by NH_4OH , NH_4HS , and $(\text{NH}_4)_2\text{CO}_3$, respectively.

The solubility in ammonium salts may be explained as follows. If an ammonium salt is brought in contact with $\text{Mg}(\text{OH})_2$, the OH' ions of the latter are withdrawn to form practically un-ionised NH_4OH , the ionisation of which is still further reduced by the excess of NH_4' ions of the NH_4Cl . More $\text{Mg}(\text{OH})_2$ therefore dissolves to provide a further supply of OH' ions, and the process goes on until the solubility product $[\text{Mg}''] \times [\text{OH}']^2$ is reached, or if this cannot be attained, until all the $\text{Mg}(\text{OH})_2$ is dissolved.

A peroxide, probably MgO_2 , is obtained in an impure state by precipitating a solution of the sulphate and hydrogen peroxide with sodium hydroxide. After drying, it is used as an antiseptic in tooth-pastes, etc.

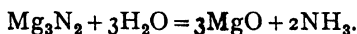
The normal magnesium carbonate MgCO_3 occurs native as *magnesite* in large amounts in Greece and in other places; the hydrate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is the rare mineral *nesquehonite*. This also slowly crystallises from a solution of 20 gm. of Epsom salt and 14 gm. of sodium bicarbonate in 150 c.c. of water. The precipitates formed by adding alkali carbonates to solutions of magnesium salts are always **basic carbonates**. From solutions at the ordinary temperature, the precipitate after drying is a light loose powder—*magnesia alba levis*, of the approximate composition

$\text{MgCO}_3, \text{Mg}(\text{OH})_2, 3\frac{1}{2}\text{H}_2\text{O}$. From a boiling saturated solution a denser crystalline precipitate is thrown down; this is evaporated to dryness, washed, and dried at 100° , and is known as *magnesia alba ponderosa*, $\text{MgCO}_3, \text{Mg}(\text{OH})_2, 3\text{H}_2\text{O}$. Both are used in medicine. Magnesium carbonate is much more easily decomposed by heat than calcium carbonate:



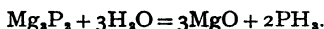
If the powdered carbonate or basic salts are suspended in water and a current of carbon dioxide is passed in, they dissolve readily, producing a bicarbonate $\text{Mg}(\text{HCO}_3)_2$. The solution is known as *fluid magnesia*. The basic carbonate is precipitated on boiling.

Magnesium nitride Mg_3N_2 is a yellow solid obtained by strongly heating magnesium in nitrogen or at a lower temperature in ammonia gas. It is decomposed by water:



Magnesium nitrate is formed as deliquescent crystals $\text{Mg}(\text{NO}_3)_2, 6\text{H}_2\text{O}$ by evaporating a solution of the oxide or carbonate in dilute nitric acid.

Magnesium phosphide Mg_3P_2 is obtained by heating magnesium and phosphorus; it is decomposed by water with evolution of phosphine:



This is used as a test for phosphates; the solid is heated with magnesium powder in an ignition tube, when magnesium phosphide is formed, and on breathing on the cooled residue a smell of phosphine is noticed.

Tertiary magnesium phosphate $\text{Mg}_3(\text{PO}_4)_2$ occurs in bones and in the seeds of cereals, and is precipitated from solutions of magnesium salts by trisodium phosphate Na_3PO_4 . Ordinary sodium phosphate Na_2HPO_4 slowly precipitates **magnesium hydrogen phosphate** $\text{MgHPO}_4, 3\text{H}_2\text{O}$, slightly soluble in cold water. On heating the solution the normal salt $\text{Mg}_3(\text{PO}_4)_2$ is precipitated, and an acid salt supposed to be $\text{MgH}_4(\text{PO}_4)_2$, derived from $2\text{H}_3\text{PO}_4$, remains dissolved. If a solution of a magnesium salt is mixed with solutions of ammonium chloride and ammonia and a phosphate added, a crystalline precipitate is deposited, slowly from dilute solutions but more rapidly on stirring or scratching the sides of the beaker with a glass rod. This consists of **magnesium ammonium phosphate** $\text{Mg}(\text{NH}_4)\text{PO}_4, 6\text{H}_2\text{O}$. This is sparingly soluble in water and less so in dilute ammonia; its formation is a test for a phosphate or magnesium. On heating to dull redness it is converted into the **pyrophosphate** $\text{Mg}_2\text{P}_2\text{O}_7$, in which form magnesium is estimated in gravimetric analysis:



Magnesium sulphide MgS is formed by direct combination. The sulphide is hydrolysed by water so that alkali sulphides precipitate only the hydroxide, but a solution probably containing the **hydrosulphide**

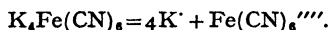
$\text{Mg}(\text{HS})_2$ is formed by passing hydrogen sulphide into a suspension of the oxide in water. It decomposes on warming, evolving *pure* hydrogen sulphide.

Magnesium sulphate occurs native as *kieserite* $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, which is practically insoluble in cold water but can be dissolved by boiling; the heptahydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ separates on cooling in colourless crystals of *Epsom salt*.

Epsom salt is also made by dissolving magnesite (native MgCO_3) or dolomite (native $\text{MgCO}_3, \text{CaCO}_3$) in boiling dilute sulphuric acid and filtering from calcium sulphate. Iron is separated by boiling with a little precipitated magnesium carbonate, and the filtrate on evaporation and cooling yields crystals of Epsom salt. Magnesium sulphate is used as a purgative, as a dressing for cotton goods, and in dyeing with aniline colours.

Several hydrates of MgSO_4 are known, *e.g.* with 7, 6, and $1\text{H}_2\text{O}$; at 150° *kieserite* ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) is formed from Epsom salt, and from *kieserite* at 200° the anhydrous sulphate. The common hydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is isomorphous with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. A monoclinic variety, isomorphous with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is known. When very strongly heated in air, magnesium sulphate decomposes, leaving the oxide. Double salts with alkali metals are readily formed, *e.g.* $\text{MgSO}_4, \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is *schönite*, a Stassfurt mineral, which is deposited from a hot solution on cooling (although K_2SO_4 is less soluble). A solution of the anhydrous sulphate in concentrated sulphuric acid deposits crystals of $\text{Mg}(\text{HSO}_4)_2$.

The **double salts** in solution are almost completely decomposed into the single salts, as is shown by the depression of freezing point. They are in this way distinguished from **complex salts** such as $\text{K}_4\text{Fe}(\text{CN})_6$, which retain their constitution in solution and ionise accordingly:



Isomorphous mixtures or **mixed crystals**, *e.g.* of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, differ from double salts by having a variable composition, and they may be represented by such formulae as $(\text{Fe}, \text{Mg})\text{SO}_4 \cdot 7\text{H}_2\text{O}$.

CALCIUM

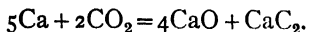
The chemistry of limestone and quicklime has been dealt with in Chapter V. In what follows, the metal calcium and its remaining compounds are considered.

Metallic calcium.—Metallic calcium was discovered by Davy in 1808. It is prepared on a technical scale by the electrolysis of fused calcium chloride.

The cathode is an iron or a water-cooled graphite rod which touches the surface of the fused chloride (Fig. 151). The cathode is slowly screwed up

as the calcium accumulates and the metal is drawn out into the form of an irregular rod, protected from oxidation by a layer of chloride.

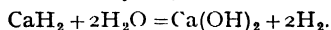
Metallic calcium is a silver-white light metal rather harder than lead. It oxidises slowly in moist air. Although it has a high boiling point, calcium readily sublimates in a vacuum at 800° . It burns brightly when heated in oxygen and combines directly with hydrogen, nitrogen, sulphur and chlorine. Calcium reduces nearly all metallic oxides and chlorides on heating; it reduces the alkali metal chlorides and fluorides on heating, but not the iodides. When rapidly heated in carbon dioxide it forms calcium oxide and carbide:



Calcium decomposes cold water slowly, evolving hydrogen, and calcium turnings are used to free absolute alcohol from the last trace of water.

CALCIUM COMPOUNDS

Calcium hydride CaH_2 is a white solid formed with incandescence on heating calcium in hydrogen; it is violently decomposed by water, with evolution of hydrogen:



Calcium fluoride or *fluorspar* CaF_2 is nearly insoluble in water, but more soluble in ammonia, ammonium salts and acids. When heated on charcoal before the blowpipe it evolves hydrofluoric acid and leaves calcium oxide.

By dissolving limestone or marble in hydrochloric acid a solution of **calcium chloride** CaCl_2 is formed. This usually contains ferric chloride as impurity, and is yellow. A little chlorine water is added to oxidise any ferrous iron, then the solution is filtered and milk of lime added until the liquid is slightly alkaline. On boiling, ferric hydroxide is precipitated; the filtered liquid is neutralised with pure hydrochloric acid and evaporated to a syrup, when colourless very deliquescent crystals of the hexahydrate $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ separate on cooling. These dissolve in water with considerable lowering of temperature and the eutectic point is -55° . On heating the crystals at 200° water is evolved and a white porous mass of the dihydrate $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ remains, which is used for preparing solutions for refrigerators. If heated more strongly a porous mass of the anhydrous salt is formed, which is used in drying gases, etc. This fuses at a red heat and forms a hard crystalline mass on cooling. The product contains a little free lime unless fused in hydrogen chloride gas. The dihydrate and the anhydrous salt evolve heat when dissolved in water. Hydrates with 4 and 1 H_2O also exist. Calcium chloride dissolves readily in alcohol. Anhydrous calcium chloride absorbs ammonia gas forming

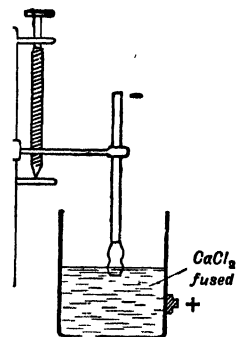


FIG. 151.

Calcium by electrolysis.

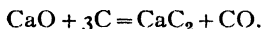
the compound $\text{CaCl}_2 \cdot 8\text{NH}_3$, which dissociates on heating, first forming $\text{CaCl}_2 \cdot 4\text{NH}_3$.

Commercial calcium chloride is made from the residues of the ammonia-soda process (p. 284).

Calcium bromide, which forms a hydrate $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$, and calcium iodide CaI_2 , which forms hydrates with 6 and 8 H_2O , are similar to the chloride.

Calcium peroxide is formed as a hydrate $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ by precipitating lime-water with hydrogen peroxide. From concentrated solutions above 40° anhydrous CaO_2 is precipitated. Calcium peroxide is manufactured for use as an antiseptic by compressing slaked lime and sodium peroxide and washing with ice-water. Much free lime is present in it. It is not formed directly from calcium oxide and oxygen (*cf.* BaO_2).

Calcium carbide CaC_2 was obtained by Wöhler in 1862 by heating carbon with an alloy of calcium and zinc. It is manufactured on a large scale by Moissan's process: a mixture of coke and quicklime is heated to a very high temperature in an electric furnace:



The furnace (Fig. 152) consists of a rectangular tank of fire-clay lined with carbon and having a graphite block in the base forming one electrode.

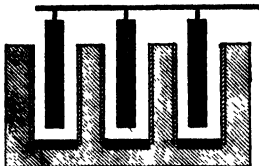
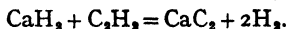


FIG. 152.—Calcium carbide furnace.

The other electrode consists of vertical blocks of carbon. Arcs are struck between the base-plate and these electrodes, and at the high temperature reaction occurs with the formation of fused carbide, which is tapped off, cooled and broken into pieces. The commercial product is a greyish-black stony mass, but pure calcium carbide, formed by heating calcium hydride in acetylene, consists of colourless transparent crystals:



Calcium carbide is decomposed by water, with evolution of acetylene:



Calcium carbide is an energetic reducing agent. A mixture of powdered carbide with ferric oxide and ferric chloride burns violently when kindled with a taper, and fused metallic iron is produced.

Commercial calcium carbide when heated in a stream of nitrogen reacts with the formation of a mixture of calcium cyanamide (p. 472) and graphite: $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$.

(On heating barium carbide in nitrogen, barium cyanide $\text{Ba}(\text{CN})_2$ is formed.)

Calcium silicide CaSi_2 is prepared from lime and excess of silicon in the electric furnace and is a hard crystalline solid, slowly attacked by water with evolution of hydrogen but rapidly by concentrated hydrochloric acid with evolution of hydrogen and silicon hydride.

Several **calcium silicates** are known and some occur as minerals, *e.g.* *wollastonite* CaSiO_3 , whilst the orthosilicate Ca_2SiO_4 and basic orthosilicate $\text{Ca}_2\text{SiO}_4 \cdot \text{CaO}$ are mixed with the aluminates $\text{Ca}_3(\text{AlO}_3)_2$ and $\text{Ca}_5(\text{Al}_3\text{O}_7)_2$ in *cement clinker*.

This is made by feeding a mixture of limestone and clay into the top of a large iron revolving furnace lined with fire-bricks and fired by a blast of air charged with powdered coal. The maximum temperature reaches

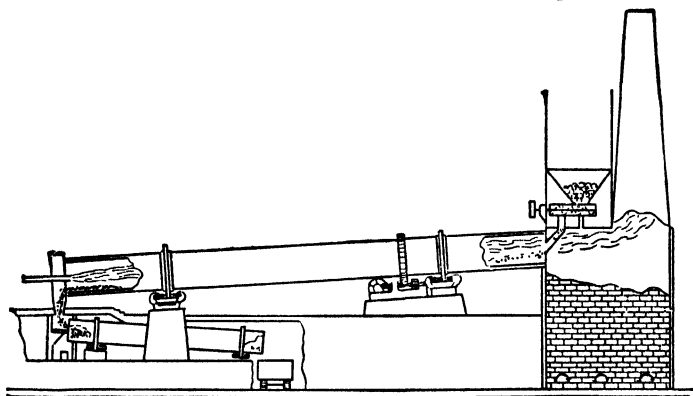
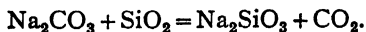


FIG. 153.—Cement furnace.

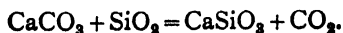
1400° . The clinker is ground to form *Portland cement*, which will set and harden under water. In the hardening the calcium silicates and aluminates are hydrated and some calcium hydroxide is formed.

Glass.—Glass was made in very early times in Egypt and Babylonia, and in the Roman period it was largely exported from Alexandria.

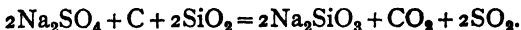
Common glass ("soda glass") contains calcium and sodium silicates and has approximately the composition $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 5\text{SiO}_2$, although it is not a definite compound but a mixture of silicates. On fusing silica with sodium carbonate a glassy mass of sodium silicate is formed on cooling, but this is soluble in water :



Calcium carbonate is similarly decomposed, but the calcium silicate, although glassy and insoluble in water, is soluble in acids :



Glass made by fusing together silica, calcium carbonate and sodium carbonate is transparent and insoluble both in water and in acids. Common *soda glass* is made by fusing pure sand, soda-ash (Na_2CO_3) and limestone in fire-clay pots or tanks. A mixture of salt-cake (Na_2SO_4) and charcoal may be used instead of soda-ash, when sulphur dioxide is evolved :



Ordinary glass always contains a small amount of aluminium oxide, perhaps derived from the crucibles. The sand used must be white and free from iron compounds for the best glass ; crushed quartz and broken flints are also used.*

Bohemian glass or *potash glass* contains potassium instead of sodium ; it has a higher melting point and greater resistance to reagents and is used for making chemical apparatus. *Flint glass* is potash glass with lime replaced by lead oxide or litharge (PbO). It has a high refractive index and is used for optical purposes, but is very soft. *Jena resistance glass* has a low alkali content and a higher alumina content (which confers toughness) than ordinary glass, and contains barium and zinc oxides, and boron trioxide in place of some silica. *Oven glass*, resistant to heat and shock, is very rich in silica, poor in alkali and alumina, and contains boron trioxide.

If glass is heated to its softening point some of the constituents slowly crystallise and the glass becomes opaque (*devitrification*). All varieties of glass require *annealing* before use : the objects are heated and allowed to cool slowly. Toughened glass has hard surfaces produced by quenching and a soft interior ; it flies to a powder when fractured and is used for motor car wind-screens.

Optical glasses for lenses may contain special constituents such as boron trioxide and phosphorus pentoxide in place of silica, barium oxide in place of lime, and sometimes zinc oxide. Two main divisions are : *crown glass* containing as basic oxide mainly potash or barium oxide, and *flint glass* containing lead oxide. By combining lenses of these two types, dispersion is eliminated. *Crookes's glass*, for spectacles, contains rare-earth compounds (praseodymium and neodymium) : it allows visible light to pass but absorbs the ultra-violet. *Vita glass* is made from materials nearly free from iron and titanium and is more permeable to ultra-violet light than ordinary glass. Ordinary glass absorbs the infra-red rays (radiant heat), hence its use for glass fire-screens.

Coloured glasses are made by adding various metallic compounds to the fused glass ; in the case of gold the colour only develops after reheating the glass for some time to increase the size of the colloidal particles present :

* Hodkin and Cousen, *Text-Book of Glass Technology*, 1925.

Ruby : gold, selenium, or cuprous oxide.

Green : chromic oxide, or cupric oxide with chromic or ferric oxides and a reducing agent.

Yellow : carbon and sulphates in the melt ; cadmium sulphide ; sometimes uranium or selenium.

Violet : manganese dioxide.

Blue : cupric oxide, cobalt oxide.

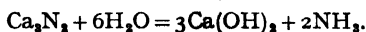
Opaque milky glass: fluorspar with felspar ; cryolite ; sometimes tin oxide or calcium phosphate.

Fluorescent greenish-yellow glass: uranium oxide.

Black glass : large quantities of ferric oxide and cupric oxide ; or cobalt, nickel and manganese oxides.

Enamels are vitrified silicate coatings applied to metal, usually cast iron or sheet steel. A "frit" is made by heating a mixture of felspar, borax, soda-ash, cryolite, fluorspar, silica and antimony and zinc oxides. It is powdered and applied mixed with water, and the goods are fired. Various colours are produced by metallic oxides (see above).

Calcium nitride Ca_3N_2 is a brownish-red solid formed when calcium is heated in nitrogen ; it is decomposed by steam :

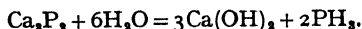


Calcium nitrate $\text{Ca}(\text{NO}_3)_2$ is present in fertile soil and is manufactured for use as a fertiliser by neutralising dilute nitric acid with limestone, or by passing oxides of nitrogen into milk of lime until the nitrite is decomposed (p. 484). Calcium nitrate decomposes on heating, evolving oxides of nitrogen and oxygen and leaving calcium oxide :



The anhydrous salt is insoluble in alcohol but dissolves in amyl alcohol ; the deliquescent crystalline hydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is soluble in alcohol, and according to T. W. Richards the best way of preparing a pure calcium salt is to recrystallise this hydrate repeatedly from water or alcohol.

Calcium phosphide Ca_3P_2 is prepared in the pure state by heating calcium with phosphorus ; with water it gives pure phosphine :



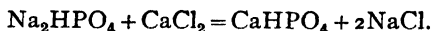
A crude phosphide mixed with calcium pyrophosphate is made by passing phosphorus vapour over heated quicklime ; it is a reddish-brown mass which with water evolves phosphine rich in the vapour of liquid phosphorus hydride P_2H_4 , hence it may contain the compound Ca_2P_3 :



Normal **calcium phosphate** $\text{Ca}_3(\text{PO}_4)_2$ occurs in bones and as the mineral *phosphorite*, and also in combination with calcium fluoride as *apatite* $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, in which part of the fluorine is sometimes replaced by chlorine as *chlor-apatite* $\text{CaCl}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$. It is formed as a flocculent precipitate by decomposing a solution of calcium chloride with ammonium phosphate and a large excess of ammonia, and is nearly insoluble in water

but is slowly decomposed by boiling water into an insoluble basic salt and a soluble acid salt (see below). It dissolves in water containing salts, *e.g.* sodium and ammonium chlorides, and carbon dioxide, hence it is dissolved from the soil and is absorbed by the roots of plants.

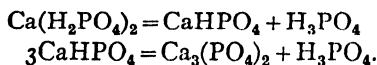
Ordinary sodium phosphate gives with excess of a solution of calcium chloride a white precipitate of **calcium hydrogen phosphate**, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (or $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) :



This and also normal calcium phosphate will dissolve in phosphoric acid and on spontaneous evaporation the solution deposits crystals of **calcium dihydrogen phosphate**, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$:

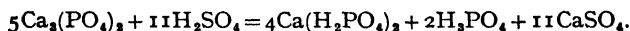


which are decomposed by water :



Pure $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (monocalcium phosphate) is made by dissolving slaked lime or limestone in pure phosphoric acid, crystallising and drying ; it is used in America in baking powder.

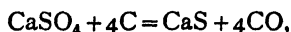
A mixture of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and CaSO_4 known as *superphosphate of lime* is prepared for use as a fertiliser by macerating ground mineral calcium phosphate in the form of phosphorites, etc., with sulphuric acid :



The reaction is carried out in a horizontal cast-iron cylinder with revolving blades inside. The mixture issues in a nearly fluid state and drops into pits or *dens*, which are half-filled and then closed. The reaction takes place with rise of temperature and gases (CO_2 , SiF_4 , HF and HCl) escape through a vent to absorption towers. After a day or two the superphosphate formed is removed by picks or mechanical elevators, powdered in a crusher, and carefully dried by hot air in long brick-work chambers. The "superphosphate" is rapidly converted in the soil into very finely divided normal phosphate which is more easily soluble than the massive form.

A "triple superphosphate", made by using concentrated phosphoric acid instead of sulphuric acid, contains 48 per cent. of P_2O_5 instead of 16 per cent. in ordinary superphosphate.

Calcium sulphide CaS is formed as *alkali waste* in the Leblanc process, or by heating gypsum to redness with charcoal :

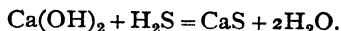


or in hydrogen : $\text{CaSO}_4 + 4\text{H}_2 = \text{CaS} + 4\text{H}_2\text{O}.$

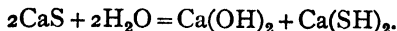
At a bright-red heat CaS reacts with CaSO_4 :



Calcium sulphide is best prepared by passing hydrogen sulphide over heated slaked lime :



It is very sparingly soluble in water but dissolves when hydrogen sulphide is passed into the suspension, forming the **hydrosulphide** which crystallises as $\text{Ca(SH)}_2 \cdot 6\text{H}_2\text{O}$. The sulphide is hydrolysed by water :



The **polysulphides** CaS_2 to CaS_5 or possibly CaS_7 are contained in the reddish-yellow solution (*thion hutor*) obtained by boiling sulphur with milk of lime.

The sulphide containing traces of heavy metals (e.g. bismuth) is phosphorescent and is used for luminous paint. Crude calcium sulphide is used as a depilatory and in removing hair from hides in tanning.

Calcium sulphite CaSO_3 is formed as a white precipitate by passing sulphur dioxide into a fairly large volume of lime-water, or by adding a solution of sodium sulphite to one of calcium chloride. It dissolves in sulphurous acid forming a solution of **calcium hydrogen sulphite** $\text{Ca(HSO}_3)_2$, used in sterilising beer casks and in the manufacture of wood-pulp. On standing exposed to air it deposits crystals of $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$.

Calcium sulphate occurs as *anhydrite* CaSO_4 along with limestone or rock-salt, or more commonly as the dihydrate *gypsum* $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which forms transparent crystals called *selenite* (often twined), or else crystalline masses, either fibrous (*satín spar*) or opaque (*alabaster*). Gypsum can easily be reduced to an extremely fine powder and the solubility increases with the fineness of the grains. The solubility of gypsum increases with rise of temperature to 40° , and then diminishes at higher temperatures.

When gypsum is heated at 125° (177° is also quoted) it loses water and forms *plaster of Paris*, the hemihydrate $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ or $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, which when mixed with water evolves heat and quickly solidifies to gypsum, expanding slightly ; it is therefore used for making casts.

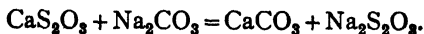
Plaster of Paris if heated at 140° begins to lose water ; the whole of the water is rapidly expelled at 200° . The residue of anhydrous CaSO_4 rapidly takes up water, but if the heating has been more intense the residue hydrates only very slowly and is said to be "dead-burnt". By heating over 400° but not too strongly a product called *Estrich plaster* is formed, which sets slowly and produces a smooth hard surface for floors and walls. *Keene's cement* is made by heating gypsum to redness, moistening with alum solution, and reheating ; it sets slowly to a hard mass.

Precipitated gypsum formed by adding sulphuric acid to a solution of calcium chloride is used under the name of *pearl-hardening* for "filling"

glazed paper. Barium sulphate (*blanc fixe*) is used for a similar purpose, giving a very heavy paper.

The double salts *syngenite* $\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, *glauuberite* $\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$ and $\text{CaSO}_4 \cdot 2\text{Na}_2\text{SO}_4$, are known. Calcium sulphate dissolves in a concentrated solution of ammonium sulphate, forming $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Strontium and barium sulphates are insoluble.

Calcium thiosulphate $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ is formed by blowing air into a suspension of the sulphide (alkali waste), or by heating the sulphite and sulphur with water. If the solution is precipitated with sodium carbonate, sodium thiosulphate is formed :



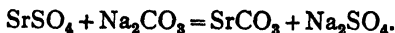
STRONTIUM

History.—A new "earth" was discovered by Crawford in 1790 in a mineral found in a lead mine at Strontian, in Argyllshire. It was further investigated by Hope in 1791, who called it *strontites*, and in 1793 by Kirwan, and by Klaproth, who called it *strontia* (see Partington, *Annals of Science*, 1942, 5, 157). The mineral is *strontianite* or strontium carbonate SrCO_3 . Another mineral is strontium sulphate or *celestine* SrSO_4 , so called from the pale-blue colour of some specimens. The element strontium occurs practically only in these two rather uncommon minerals. Metallic strontium was discovered by Davy in 1808.

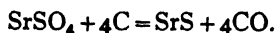
Strontium and its compounds. Metallic strontium is prepared by the electrolysis of the fused chloride, by heating the oxide with aluminium, and by preparing strontium amalgam by electrolysis with a mercury cathode and driving off the mercury at a high temperature in hydrogen (when the hydride is first formed and then decomposes). It is a silver-white soft metal which oxidises very easily in air, burns in oxygen, and decomposes water.

Strontium hydride SrH_2 is formed by strongly heating the metal in hydrogen and is a white solid resembling calcium hydride in its properties.

Strontium chloride $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ is a colourless crystalline salt, efflorescent in air (it is much less soluble in water than calcium chloride). It is prepared by dissolving native strontium carbonate in hydrochloric acid, oxidising any iron with chlorine and digesting with some strontium carbonate precipitated from some of the solution by sodium carbonate, when ferric oxide is precipitated; the liquid is filtered, evaporated and crystallised. It may also be prepared from the native sulphate by fusing with sodium carbonate, when strontium carbonate is formed, which is washed with water and dissolved in hydrochloric acid :

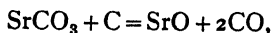


The sulphate may also be heated with carbon when strontium sulphide is formed, which is dissolved in hydrochloric acid :

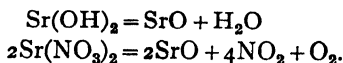


Anhydrous strontium chloride is only sparingly soluble in absolute alcohol; calcium chloride is readily soluble, whilst barium chloride is practically insoluble in ethyl alcohol but dissolves in methyl alcohol. (The bromides and iodides of strontium and barium are readily soluble in alcohol.)

Strontium oxide (*strontia*) SrO is obtained by strongly heating the carbonate, more readily when mixed with carbon :

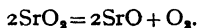


or at a red heat from the hydroxide and nitrate :



It is a white mass which combines with water with evolution of heat to form the hydroxide Sr(OH)_2 . This forms a readily soluble crystalline hydrate $\text{Sr(OH)}_2 \cdot 8\text{H}_2\text{O}$, which effloresces to a hydrate with $1\text{H}_2\text{O}$ and at 100° this gives Sr(OH)_2 . Like calcium hydroxide and unlike barium hydroxide, strontium hydroxide forms the oxide at a dull-red heat. The hydroxide is used in sugar refining, since it forms a sparingly soluble compound $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$ with cane sugar, which can so be separated from the molasses.

Strontium peroxide SrO_2 is formed at a dull-red heat from the oxide and oxygen but only *under pressure*. It is similar to barium peroxide. A crystalline hydrate $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$ is precipitated in pearly scales on adding hydrogen peroxide to a solution of strontium hydroxide; on heating gently it gives SrO_2 which decomposes at a higher temperature :



Strontium carbonate is precipitated from a solution of a strontium salt by sodium carbonate; it dissolves in water containing carbonic acid to form a bicarbonate.

Strontium nitride Sr_3N_2 is formed by heating the metal in nitrogen. It is black and is readily decomposed by water, evolving ammonia.

Strontium nitrate $\text{Sr(NO}_3)_2$ crystallising anhydrous from hot concentrated solutions is prepared by dissolving the carbonate in dilute nitric acid; it is used mixed with sulphur and charcoal to make "crimson fire" for fireworks. It is insoluble in alcohol and amyl alcohol and less soluble in water than calcium nitrate. Strontium nitrate is freed from barium by adding calcium sulphate solution (which precipitates barium sulphate), filtering and crystallising.

Strontium sulphate SrSO_4 is sparingly soluble in water (0.1 gm. per lit.) but soluble in dilute hydrochloric acid; it is insoluble in ammonium sulphate solution, but is more soluble in strontium nitrate solution than in water. Unlike calcium sulphate it does not form a hydrate. It is less soluble than calcium sulphate and a saturated solution of calcium sulphate gives a precipitate with a strontium salt.

Strontium salts impart a splendid crimson colour to the bunsen flame, and it is interesting that the spectrum of the flame (that of crimson fire in a theatre) had been examined by Fox Talbot in 1826 long before Bunsen and Kirchhoff invented spectrum analysis.

BARIUM

History.—The heavy mineral "heavy spar" (density = 4.5) is found associated with metallic ores such as galena; it is barium sulphate BaSO_4 . Early in the seventeenth century * a shoemaker of Bologna found that when strongly heated with charcoal this stone produces a material which is phosphorescent after exposure to light; barium sulphide is formed:



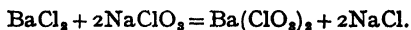
Scheele in 1774 showed that heavy spar is the sulphate of an "earth" which was called *barote* (Greek, *barys* = heavy) by Guyton de Morveau and *barytes* by Kirwan. Metallic barium was obtained by Davy in 1808 from the amalgam formed by electrolysis.

Occurrence.—Barium occurs as *barytes* or *heavy spar*, the sulphate BaSO_4 ; as *witherite*, the carbonate BaCO_3 (isomorphous with aragonite and a common gangue material in lead mines); as *alstonite* BaCO_3 , CaCO_3 in rhombic crystals and in monoclinic crystals as *baryto-calcite*. Barium also occurs as an impurity in some other ores, e.g. of manganese (*psilomelane*, see p. 583).

Barium and its Compounds.—Metallic barium is prepared by processes analogous to those used for strontium; very pure barium is obtained by the slow distillation of the dry amalgam (obtained by electrolysis with a mercury cathode), when mercury first distils and then barium. It is a silver-white soft metal which inflames spontaneously in air and decomposes water and alcohol. A hydride BaH_2 is formed at a bright red heat.

Barium chloride BaCl_2 is prepared from the native carbonate and sulphate by methods analogous to those used for strontium chloride. A large excess of sodium carbonate must be used in decomposing the barium sulphate, and a high temperature in its reduction with carbon. Barium chloride crystallises as $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and the crystals are neither efflorescent nor deliquescent. It is readily soluble in water but insoluble in absolute alcohol, and is almost insoluble in concentrated hydrochloric acid, which precipitates it from solution.

Barium chlorate $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ is used in the preparation of chloric acid (p. 168) and is made by evaporating a solution of sodium chlorate and barium chloride, when sodium chloride is deposited:

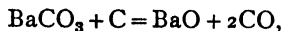


The solution is filtered through a hot-water funnel and further evapor-

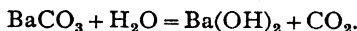
* According to Licetus, *Litheosphorus, sive de Lapide Bononiensi*, 1640, p. 12, the discovery was made in 1602 by Vincent Casciorolo.

ated, when the barium chlorate crystallises on cooling. It is purified by recrystallisation.

Barium oxide (*baryta*) BaO is best obtained by heating the nitrate strongly (to decompose any peroxide formed), or the iodate (when a periodate is first formed). Barium carbonate is only slightly decomposed even at a bright-red heat (it attacks platinum at a red heat) unless mixed with charcoal :

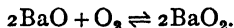


or heated in a current of steam, when the hydroxide is formed :



Barium oxide combines vigorously with water with evolution of heat to form the **hydroxide** $\text{Ba}(\text{OH})_2$; this gives a crystalline hydrate with $8\text{H}_2\text{O}$ readily soluble in hot water. On exposure to air free from carbon dioxide the crystals effloresce to $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, and at 100° $\text{Ba}(\text{OH})_2$ is formed. This fuses on heating and (unlike calcium and strontium hydroxides) does not lose water completely even at a high temperature. A solution of barium hydroxide in water (*baryta water*) gives a white precipitate of barium carbonate with carbon dioxide, soluble in excess to form a bicarbonate decomposed on boiling. Barium hydroxide is a strong base and is sometimes used in volumetric analysis instead of sodium hydroxide, since any carbonate formed on exposure to air is precipitated and does not interfere with the colour-changes of some indicators. Baryta forms a sparingly soluble compound with cane sugar, but is not used in sugar refining since barium salts are poisonous.

Barium peroxide BaO_2 is readily formed by passing oxygen or air free from carbon dioxide over barium oxide at a dull-red heat; at a bright-red heat it decomposes into oxygen and barium oxide :



A crystalline hydrate with $8\text{H}_2\text{O}$ is formed by adding hydrogen peroxide to baryta water, and when gently heated it forms the anhydrous peroxide. By adding baryta water to hydrogen peroxide the compounds $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ (yellow) and $\text{BaO}_2 \cdot 2\text{H}_2\text{O}_2$ are precipitated.

Barium carbonate BaCO_3 is formed as a white precipitate on adding an alkali carbonate to a solution of barium chloride. It is more soluble (0.02 gm. per lit.) than strontium carbonate (0.01 gm. per lit.) and is slightly hydrolysed in solution; a suspension of barium carbonate is sometimes used in qualitative group separation as it precipitates ferric, chromic and aluminium hydroxides from solutions of their salts, but not zinc or manganese salts. Barium carbonate is stable at a high temperature.

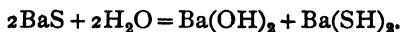
Barium nitride Ba_3N_2 is a black solid formed by heating barium in nitrogen; it evolves ammonia with water.

Barium nitrate $\text{Ba}(\text{NO}_3)_2$, which crystallises anhydrous, is made by dissolving the carbonate in dilute nitric acid. It is much less soluble in water than strontium nitrate and is insoluble in alcohol and in nitric acid,

which precipitates it from solution. A pure barium compound is best obtained by repeated crystallisation of the nitrate ; from the pure nitrate the carbonate is precipitated with ammonium carbonate and is then dissolved in an acid to form the corresponding salt. Barium nitrate mixed with charcoal and sulphur forms "green fire" in pyrotechny ; barium salts give an apple-green flame when heated on platinum wire in the bunsen flame.

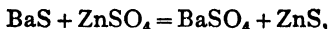
Barium nitrite $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ is prepared by mixing hot nearly saturated solutions of sodium nitrite and barium chloride, filtering from the sodium chloride with a hot-water funnel, and allowing to crystallise. The salt is recrystallised from water and dried over sulphuric acid. It is very soluble.

Barium sulphide BaS is obtained by reducing the sulphate with carbon (see above), but most conveniently by the action of hydrogen sulphide on gently heated $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$; it is easily soluble and is hydrolysed :



Polysulphides of barium and strontium are known.

Barium sulphate BaSO_4 is formed by adding dilute sulphuric acid or a solution of a sulphate to a solution of a barium salt, as a fine white precipitate nearly insoluble in water (2.4 mgm. per litre) and acids, except hot concentrated sulphuric acid which forms the acid sulphate $\text{Ba}(\text{HSO}_4)_2$, or in hot very concentrated hydrochloric acid. Precipitated barium sulphate is used as a pigment (*blanc fixe* or *permanent white*), but has a poor covering power. *Lithopone* is a mixture of barium sulphate and zinc sulphide and oxide made by precipitation :



and heating the precipitate. It has a good covering power, and does not darken on exposure to hydrogen sulphide, but darkens on exposure to light.

Barium sulphate carries down from solution various soluble salts, especially potassium sulphate and sulphates, salts of tervalent metals (Fe, Cr), nitrates, and chlorates, which cannot be removed by washing. It also adsorbs barium chloride and is slightly soluble in dilute hydrochloric acid and in many salt solutions. Barium sulphate is only slightly decomposed at a white heat. These properties are of importance in quantitative analysis. Barium and strontium sulphates are converted into carbonates by boiling with alkali carbonate, and the reaction is reversible. Barium sulphate is almost quantitatively converted to carbonate on fusion with 8-9 mols. of potassium carbonate, but barium carbonate is only very incompletely converted into sulphate on fusion with potassium sulphate.

The atomic weights of magnesium, calcium, strontium and barium have been determined by precipitating the chlorides or bromides with silver nitrate. The valencies follow from the atomic heats of the metals.

CHAPTER XXIV

ZINC, CADMIUM AND MERCURY

ZINC

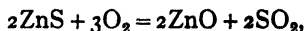
History.—Brass of the period 1500 B.C. containing 23 per cent. of zinc and 10 per cent. of tin, was found at Gezer in Palestine. Deposits of *calamine*, native zinc carbonate, occur in the old silver mines of Laurion in Greece. Strabo (about 7 B.C.) describes the preparation of the metal, which he calls mock-silver, by heating the oxide with coal. Several early specimens of zinc are known, including bracelets from Rhodes (5th cent. B.C.), pure hammered sheet from Athens (not later than 250 B.C.), and a statuette from Thrace (1st cent. A.D. or earlier). Zinc was known fairly early in India.

The name *spelter* is used for the metal by Boyle, and Libavius about 1600 describes zinc, which he says was a peculiar kind of tin called *calaēm* brought from the East Indies. Zinc was extracted from calamine in Bristol in 1685 and exported to Sweden. The extraction was studied by Isaac Lawson in 1730, and in 1743 the first European zinc works was started by John Champion at Bristol, near where the metal is still made.

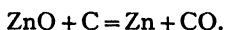
Occurrence.—Zinc occurs as *blende* (*sphalerite* in the U.S.A.) ZnS , usually coloured yellow or brown by iron ("black-jack" of the miners), with a resinous lustre. It is found in England, in many parts of Europe and America, in Rhodesia, Burma and New South Wales. The carbonate occurs as *calamine* or *smithsonite* ZnCO_3 . *Siliceous* (or *electric*) *calamine* or *hemimorphite* is a silicate $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$. The anhydrous silicate is *willemite*, which is used in making fluorescent screens in X-ray work and radioactivity. The oxide *zincite* or *red zinc ore* ZnO is rare, but the ferrite $\text{Zn}(\text{FeO}_2)_2$ or $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ forms the important *franklinite* deposit of Franklin Furnace, New Jersey, mostly worked for zinc oxide and the manganese it contains. The New South Wales ore contains galena and is first "concentrated" by flotation (p. 269). Certain varieties of pyrites, *e.g.* Westphalian, contain zinc sulphide. Traces of zinc occur as an organic compound in animal cells and in snake venom.

Metallurgy.—Zinc is a volatile metal and can be distilled. In 1807 zinc smelting was begun at Liège in Belgium and later on spread to Silesia. These two processes are still in use and are called the **Belgian process** and the **Silesian process**, respectively.

The blende is first roasted and the sulphur dioxide produced may be used to make sulphuric acid. External heating has to be applied, the blende being raked in a series of muffles through which air circulates, or on a furnace hearth. Care must be taken that only zinc oxide is produced :



since the sulphate is very stable and would give sulphide in the subsequent reduction, leading to considerable loss. Some sulphate which is always formed is decomposed at the high temperature used. The roasted ore is next mixed with half its weight of powdered coal and charged into small fire-clay retorts which are strongly heated. Zinc distils off :



The Belgian retorts consist of fire-clay tubes closed at one end and set in a furnace, sloping towards the open end. An iron tube (called a "prolong") is luted into the open end with clay and serves to condense the zinc. The Silesian retorts (Fig. 154) are fire-clay muffles, to which a fire-clay



FIG. 154.—Zinc furnace.

condenser tube and an air-cooled iron "prolong" are luted. The newer Belgo-Silesian furnaces employ three rows of muffles, one above the other, the lower row supported along their length on the hearth and the two upper rows only at the ends. They are fired with gas. In all cases 10-25 per cent. of the zinc is lost, about half in the ash and half as vapour, and a considerable proportion of the metal is obtained in the form of a powder mixed with oxide known as *zinc dust*. Continuous vertical furnaces are coming into use and sometimes the poor grade oxidised ores are roasted to form zinc oxide fume which is collected and then reduced in retorts.

Commercial zinc is called *spelter* and contains about 97-98 per cent. of zinc, 1-3 per cent. of lead, up to 0.1 per cent. of iron, more rarely cadmium and some arsenic. Pure zinc is prepared by electrolysis of an acid solution of pure zinc sulphate with a high current density. It is essential that the electrolyte shall be free from cobalt. Indium is recovered as a by-product from some ores. The electrolyte may be prepared from roasted blende, dissolved in dilute sulphuric acid, followed by purification of the solution.

Very pure zinc (99.99 per cent.) is made by rectification distillation. The main impurities are iron (b.p. 2800°), lead (b.p. 1620°) and cadmium (b.p. 767°). The cadmium can be completely vaporised below the boiling point of zinc (905°). Molten zinc is fed into a column heated above its

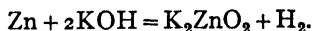
boiling point when most of the zinc and all the cadmium distil and are condensed, the iron and lead collecting in the metal flowing from the base of the column. The molten zinc-cadmium alloy is similarly treated in a second column, when cadmium distils off and pure zinc flows from the base of the column.

For use in the laboratory zinc is granulated by melting in a clay crucible and pouring into a bucket of water. Zinc foil or sheet is prepared by heating the metal to 100° - 150° , when it becomes soft, and rolling it.

Properties.—Zinc, which is crystalline, moderately hard and brittle, has a bluish-white colour. Its vapour density corresponds with the formula Zn. It readily burns in air when the turnings are heated in a flame, or the metal is heated strongly in a crucible, producing a white cloud of oxide which settles out in the form of woolly flocks. These were called "Philosophers' wool", *nix alba*, or *pompholyx*, by the alchemists. A tassel of thin sheet zinc tipped with a little burning sulphur burns brilliantly in oxygen. The metal oxidises in moist air forming a greyish-white crust of the basic carbonate, and is attacked and dissolved by soft water, especially that containing peat acids, or sea water.

Zinc is more resistant to moist air than iron, and is used as a protection for this metal. The iron sheets or wire are cleaned by a sand-blast and "pickling" in dilute hydrochloric acid, and are dipped into molten zinc when an adherent coating of the latter is formed. This process is known as *galvanising* and the product as *galvanised iron*. Iron articles may also be coated with zinc by spraying or by heating them in zinc dust (*sherardising*). The zinc dissolves before iron in presence of oxygen and moisture, since it is more electropositive than iron. The metal is also used for the negative electrodes of voltaic cells.

Zinc dissolves in dilute acids evolving hydrogen (except with nitric acid) and producing zinc salts containing the cation Zn^{++} . It also dissolves readily in hot solutions of potassium or sodium hydroxides (magnesium is insoluble), evolving hydrogen and forming solutions of *zincates*:



Ordinary zinc dissolves readily in dilute acid, whereas some varieties of very pure metal dissolve slowly unless a few drops of copper sulphate or platinic chloride solution are added. Metallic copper or platinum is precipitated on the zinc and forms a galvanic couple, from the insoluble part of which hydrogen is readily evolved. Sturgeon (1830) found that the amalgamated metal is hardly attacked by acids; the commercial varieties are more resistant when amalgamated than the amalgamated pure metal (J. N. Friend, 1929).

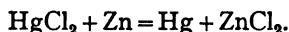
Copper and zinc form two definite compounds Cu_2Zn , and (probably) CuZn , and also two types of solid solutions called α - and β -brass. The

brasses are of two main types : (1) those with more than 64 per cent. of copper, which are homogeneous α -solutions ; (2) those with 55-64 per cent. of copper, composed of α - and β -solutions. Brasses of 70 copper + 30 zinc typify (1) and those of 60 copper + 40 zinc typify (2).

The effect of adding zinc to copper is to increase progressively the strength, toughness and hardness of the alloy up to 36 per cent. of zinc, after which the increase in strength is more marked. Zinc mixes when fused with tin, copper and antimony in all proportions, but is only partially miscible with lead and bismuth.

ZINC COMPOUNDS

Anhydrous zinc chloride is a soft white mass, subliming at a red heat in white needles, formed by passing chlorine or hydrogen chloride over heated zinc or by distilling the metal with mercuric chloride :



Chlorine decomposes zinc oxide at a dull-red heat forming the chloride with evolution of oxygen. Zinc chloride is formed in solution by dissolving zinc or its oxide in concentrated hydrochloric acid. On evaporation a syrupy liquid is obtained ; if a little concentrated hydrochloric acid is added to this, small deliquescent crystals of $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ separate. If the aqueous solution is evaporated to dryness, the oxychlorides $\text{Zn}(\text{OH})\text{Cl}$ and Zn_2OCl_2 are formed to some extent, but if the dry mass is distilled at a red heat the anhydrous chloride passes over. By evaporation in a current of hydrochloric acid gas the fused salt is obtained and may be cast into sticks. Zinc chloride is very deliquescent and is soluble in water, alcohol, ether, acetone and pyridine.

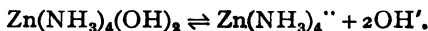
An oxychloride is produced by mixing the syrupy solution of the chloride with zinc oxide, when the whole sets rapidly to a very hard mass which is used as a cement. The concentrated solution of zinc chloride is used for impregnating timber to prevent its destruction by micro-organisms ("dry rot"), and as a caustic (it dissolves proteins). In timber-preserving zinc chloride is being replaced by sodium fluoride.

A solution of zinc chloride is used as a flux in soldering. On heating it liberates hydrochloric acid, which dissolves metallic oxides and keeps the metal surface clean. Zinc chloride is used, like magnesium chloride, for "filling" (*i.e.* weighting) cotton goods. The salt $\text{ZnCl}_2 \cdot 2\text{NH}_3$ is formed as crystals in Leclanché batteries, and zinc chloride absorbs ammonia gas to form a number of compounds, *e.g.* $\text{ZnCl}_2 \cdot 4\text{NH}_3$. These are hydrolysed by water, with deposition of white oxychlorides which dissolve in dilute hydrochloric acid.

Zinc bromide and iodide are formed from the elements in presence of water. Zinc fluoride $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ is sparingly soluble.

Zinc oxide ZnO is produced by the combustion of the metal; when so prepared it is called *zinc white* and is used as a pigment. It is prepared for pharmaceutical purposes by precipitating a solution of zinc sulphate with sodium carbonate and heating the basic carbonate. It is a white powder which becomes sulphur-yellow on heating, the colour disappearing on cooling. A crystalline oxide is formed by the action of steam on zinc at a red heat. Zinc oxide sublimes appreciably above 1000° . It is reduced by hydrogen above 450° . Zinc oxide dissolves readily in acids producing zinc salts, and in alkalis forming *zincates*, e.g. $\text{Na}_2\text{ZnO}_2 \cdot 4\text{H}_2\text{O}$ and $\text{NaHZnO}_2 \cdot 3\text{H}_2\text{O}$, which can be obtained in the solid state. It is therefore an *amphoteric oxide* (p. 43).

Zinc hydroxide Zn(OH)_2 is formed as a white flocculent precipitate on adding an alkali hydroxide to a solution of a zinc salt. Crystals are obtained by allowing a zinc plate and iron turnings to stand in concentrated ammonia. It can be dried at 85° but loses water at higher temperatures. Zinc hydroxide is practically insoluble in water, but the precipitate is readily soluble in excess of alkali, forming a solution of a zincate. Ammonia also dissolves it, forming a complex hydroxide:



Zinc oxide is used as an absorbent in surgical dressing, as a "filling" for rubber, and in the preparation of *Rinman's green*, which is obtained by heating zinc oxide with a solution of cobalt nitrate and is cobalt zincate CoZnO_3 in solid solution in zinc oxide. The formation of this green substance is the basis of the blowpipe test for zinc.

By the action of cooled 30 per cent. hydrogen peroxide on zinc oxide, a white or yellow powder is obtained, which is believed to be a hydrated peroxide $\text{ZnO}_2 \cdot \text{Aq}$.

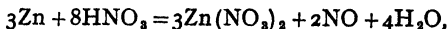
Sodium carbonate precipitates white **basic zinc carbonate** from a solution of a zinc salt; the composition depends on the concentrations and temperature but is approximately $\text{ZnCO}_3 \cdot 2\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$. A solution of an alkali bicarbonate gives a white precipitate of **zinc carbonate** ZnCO_3 , soluble in a concentrated solution of potassium carbonate but precipitated on dilution. A crystalline carbonate is formed by heating a solution of the sulphate with sodium bicarbonate in a sealed tube. When boiled with sodium carbonate solution, the carbonate or basic carbonates form zinc oxide. Zinc and zinc oxide dissolve in water containing carbon dioxide.

Zinc nitrate $\text{Zn(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is obtained by dissolving the metal, oxide or carbonate in dilute nitric acid and crystallising. It is deliquescent and is soluble in alcohol.

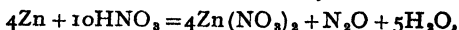
The action of nitric acid on zinc is complex ; with concentrated acid nitrogen peroxide is evolved :



with diluted acid, nitric oxide :



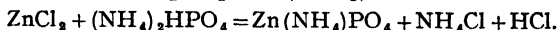
whilst with very dilute acid nitrous oxide may be evolved :



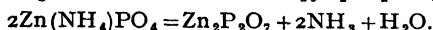
and some acid is also reduced to ammonium nitrate :



Zinc phosphate $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is obtained by heating a solution of zinc sulphate and Na_2HPO_4 , in the form of pearly scales insoluble in water and dilute acids. On heating it forms the infusible anhydrous salt. Zinc ammonium phosphate $\text{Zn}(\text{NH}_4)\text{PO}_4$ is precipitated from neutral solutions of zinc salts by ammonium phosphate (cf. Mg) :



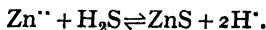
On heating to bright redness it forms zinc pyrophosphate, $\text{Zn}_2\text{P}_2\text{O}_7$:



A mixture of zinc oxide and syrupy phosphoric acid, forming basic zinc phosphate, is used as a dental cement.

Zinc sulphide ZnS occurs in regular cubic crystals as *blende* and more rarely in hexagonal crystals as *wurtzite*. Wurtzite may be formed from zinc vapour and hydrogen sulphide. An artificial phosphorescent sulphide (*Sidor's blende*) formed on heating the precipitated sulphide to whiteness in a covered crucible is used in making fluorescent screens for X-ray and radioactivity work. Perfectly pure zinc sulphide is not fluorescent. Massive zinc and sulphur do not react easily on heating, but the mixed powders react with incandescence when heated and the mixture may detonate on percussion. Zinc sulphide is easily obtained by heating zinc oxide with sulphur or as a white precipitate on adding ammonium sulphide to a solution of a zinc salt ; it is insoluble in excess of reagent but dissolves in all dilute mineral acids, but not in acetic acid (cf. MnS).

If hydrogen sulphide is passed into a solution of zinc sulphate, zinc sulphide is at first precipitated but owing to the acid formed the precipitation soon ceases :

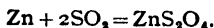


If sodium acetate is added to the solution, the concentration of hydrogen ions is kept low by the formation of the very weak acetic acid :



If nickel and cobalt are present, they are precipitated only after all the zinc has been thrown down.

Zinc dissolves in sulphurous acid solution to form a hyposulphite ("hydro-sulphite") ZnS_2O_4 which is a powerful reducing agent :



Zinc sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, isomorphous with Epsom salt, is known as *white vitriol* and is very soluble in water. It is the commonest salt of zinc and is prepared by dissolving the metal, oxide or carbonate in dilute sulphuric acid, evaporating, and crystallising below 30° . Above 30° $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ is deposited. On heating $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at 100° $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ is left, which loses water only at 450° . When strongly heated, sulphur trioxide is evolved and a basic salt, or at a higher temperature zinc oxide, remains. Double salts, e.g. $\text{K}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$, are easily prepared. A dilute solution of white vitriol is used as an eye lotion, and zinc sulphate is used in the manufacture of lithopone (p. 348).

Ammine compounds similar to those of copper are formed with zinc salts, e.g. $\text{Zn}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{NH}_3)_5\text{SO}_4$, etc.

The atomic weight of zinc was determined by precipitating pure zinc bromide with silver nitrate.

CADMIUM

History.—A certain specimen of zinc oxide which had a yellow colour, although free from iron, was found by Stromeyer in 1817 to contain the oxide of a new metal to which he gave the name cadmium, from *cadmia*, the old name for zinc ore (*καδμεια*, in Dioskurides).

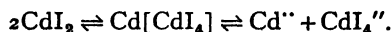
Occurrence.—Most zinc ores contain small amounts of cadmium. The only mineral, the sulphide *greenockite* CdS , is rare.

Cadmium and its compounds.—Cadmium is more volatile than zinc, as the boiling points of the metals in the zinc group decrease with rising atomic weight. Hence the first portions of dust collecting in the receivers of zinc furnaces in which ores containing cadmium are reduced contain most of the cadmium in the form of brown oxide CdO , mixed with zinc oxide. The dust is heated strongly with coal in retorts having long sheet-iron tubes as adapters. The distillate is enriched in cadmium oxide and is distilled with charcoal in small iron or clay retorts to give the metal. In America much cadmium is extracted from the fumes from lead and copper furnaces, and some from the solutions used in making electrolytic zinc, from which it is precipitated by zinc.

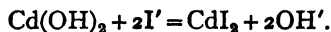
Cadmium is a soft bluish-white metal of low melting point. The vapour density corresponds with the formula Cd . It is slowly oxidised in air, forming a protective coating, and very thin deposits of plating are used to protect iron and steel from rust. They may be heat-treated to form an alloy with the iron. Cadmium is a constituent of some fusible alloys (p. 537). A small amount of cadmium is alloyed with copper for electricity transmission wires ; it is added in small amounts to aluminium

for casting and is also added to silver to decrease staining. It is used in antifriction alloys and in solders in place of tin. Cadmium amalgam, formerly used for dental fillings, forms the cathode in the Weston standard cell.

Cadmium dissolves slowly in dilute hydrochloric, sulphuric and nitric acids, forming colourless salts. The chloride $2\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ is efflorescent and is not hydrolysed by water. The halogen salts are all soluble in water but they are only feebly ionised in solution, forming complex ions in which the metal exists in the negative ion :



Insoluble cadmium salts, *e.g.* CdS , therefore readily dissolve in a solution of potassium iodide, since practically all the cadmium ions are removed as complex ions or un-ionised salt and the solubility product of the salt is not exceeded :



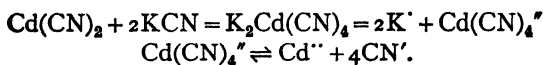
If a concentrated solution of potassium iodide is added to an ammoniacal solution of a cadmium salt, a white precipitate of $\text{Cd}(\text{NH}_3)_2\text{I}_2$ is formed. Copper gives no precipitate. Cadmium iodide is used in photography.

The brown **cadmium oxide** CdO is formed by burning cadmium in air, or by heating the hydroxide, carbonate or nitrate.

The white **cadmium hydroxide** $\text{Cd}(\text{OH})_2$ is precipitated by alkali hydroxide from a solution of the nitrate or sulphate; it is insoluble in excess but dissolves in ammonia forming a complex hydroxide $\text{Cd}(\text{NH}_3)_4(\text{OH})_2$.

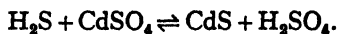
Cadmium hydroxide attracts carbon dioxide from the air and the normal **carbonate** CdCO_3 is precipitated by adding excess of ammonium carbonate to a solution of cadmium chloride, then just enough ammonia to dissolve the precipitate and heating on the water bath. The white precipitate thrown down by alkali carbonates from solutions of cadmium salts is of variable composition, as in the case of zinc.

Cadmium cyanide $\text{Cd}(\text{CN})_2$ readily forms a soluble complex salt with potassium cyanide, but the complex ion is so much ionised that a precipitate of cadmium sulphide is thrown down from the ammoniacal solution by hydrogen sulphide (*cf.* copper, p. 312) :



Cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is deliquescent and is soluble in alcohol.

Cadmium sulphide CdS is obtained as a bright-yellow precipitate (used by artists under the name of *cadmium*) by passing hydrogen sulphide through a solution of a cadmium salt which is not too strongly acid. It crystallises in forms which may be either yellow or red. In more acid solutions a *red* form is precipitated—perhaps only because the particles are larger. If the acid concentration exceeds 1.3 normal the sulphide is not precipitated :



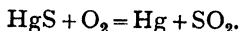
According to Treadwell, a double salt, *e.g.* $\text{Cd}_2\text{Cl}_2\text{S}$, is always present in the precipitate. Cadmium sulphide is insoluble in ammonium sulphide but is soluble in boiling dilute sulphuric acid.

Cadmium sulphate $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ is formed in large crystals by the spontaneous evaporation of a solution of cadmium or cadmium oxide in dilute sulphuric acid. It is used in the solution in the Weston cell.

MERCURY

History.—Metallic mercury is mentioned by Aristotle and Theophrastos as "liquid silver" and Dioskurides calls it "silver water" or *hydrargyros*, which Pliny calls *hydrargyrum* (the origin of the symbol Hg). The name "quicksilver" (*argentum vivum*) is also used by Pliny. In the Roman period the metal was made, as at present, by heating the native sulphide from Spain, which was also used as a red pigment.

Metallurgy.—Small quantities of mercury occur native or as amalgams and halogen compounds, but the only important ore is *cinnabar*, mercuric sulphide HgS , a red or black mineral found in Almaden (Spain), Idria, Monte Amiata (Italy), and in smaller amounts in Peru, California, Mexico, China, and Japan. In the extraction of the metal the cinnabar is roasted in a current of air:



The metal is not easily oxidized and its vapour is condensed.

In modern works the lump ore is mixed with fuel and fed to the top of a shaft furnace (Fig. 155) and the mercury vapour is condensed in cooled Y-shaped tubes. Powdered ore is roasted in a vertical shaft with inclined shelves sloping alternately in opposite directions, flames and heated air passing upwards over the ore, and the mercury vapour is condensed in brick chambers and flues.

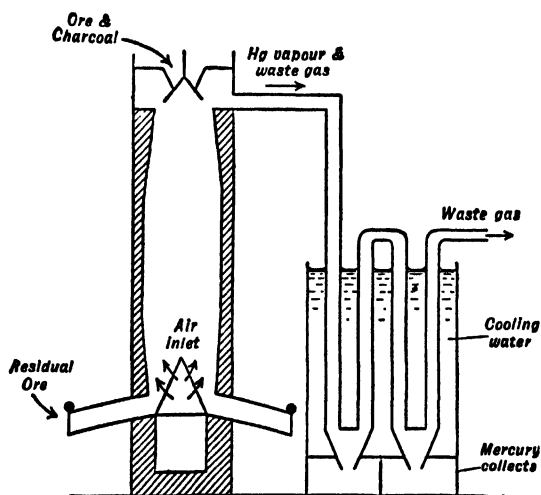


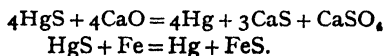
FIG. 155.—Mercury shaft furnace.



FIG. 156.—
Purification
of mercury.

In the older process of extraction, now used only at Almaden, the ore is roasted in a shaft by a fire, and the vapours pass through openings into series of stoneware *udells* arranged first in a descending and then in an ascending position on brick arches. The condensed mercury flows from these into a channel and then into cisterns. The metal is exported in iron bottles holding about 75 lb.

The old processes in which cinnabar was distilled with lime or iron filings are in use only for very rich ore :



Commercial mercury contains lead and sometimes zinc, tin and bismuth; it leaves a "tail" when it runs over glass and forms a black scum when shaken with air. It is purified by running it several times in a fine stream through a column of 5 per cent. nitric acid containing some mercurous nitrate (Fig. 156), when the lead, etc. (which are more easily oxidised than mercury) dissolve in the acid; it may also be shaken with a concentrated solution of potassium permanganate in 6*N* sulphuric acid containing a little ferric chloride. The mercury is then distilled in a vacuum with a still surface, as if it "bumps" impurities are carried over (Fig. 157).

Properties.—Mercury is a silver-white liquid metal of high density which freezes to a malleable solid in solid carbon dioxide and ether. It boils at 357° and the vapour is monatomic (see p. 89). The metal has only a small vapour pressure at room temperature and in laboratory air it is covered with a film so that it is practically non-volatile. The vapour may be seen rising from warm mercury by its fluorescence in ultra-violet light, and as it is very poisonous mercury should never be heated in an open vessel in the laboratory.

Mercury is used in making thermometers and barometers, mercury vapour lamps, and amalgams; its compounds (especially mercuric oxide and mercurous and mercuric chlorides) are used in medicine, and the fulminate is used in detonators.

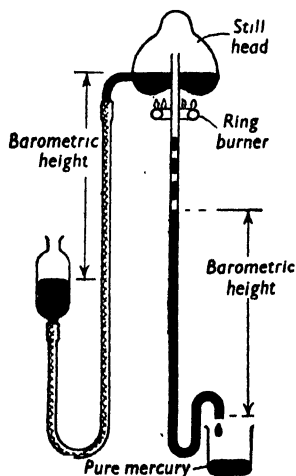


FIG. 157.—Mercury still.

When triturated with fats and powders such as chalk or sugar, mercury is divided into very minute globules and such grey preparations are used in medicine. A brown colloidal solution is formed by reducing mercurous nitrate by stannous nitrate in presence of ammonium citrate.

Mercury forms amalgams with most metals and these often contain definite compounds; iron is amalgamated with difficulty, by grinding iron powder with water and mercuric chloride. Copper amalgam becomes plastic when warmed at 100° and rubbed in a mortar; it hardens again after a few hours and is used in filling teeth. Mercury in silver nitrate solution forms a tree-like growth (*arbor Dianae*) of silver amalgam. Mercury easily whitens gold and copper.

Mercury combines with oxygen and sulphur when heated, with chlorine at the ordinary temperature, and with iodine on grinding in a mortar; with excess of mercury green mercurous iodide is formed, with excess of iodine red mercuric iodide. The metal is not attacked by hydrochloric acid in absence of air nor by cold concentrated or hot dilute sulphuric acid. Hot concentrated sulphuric acid converts it into mercuric sulphate. Mercury is dissolved by dilute and concentrated nitric acid, forming mercurous and mercuric nitrates, respectively.

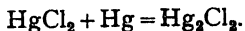
Mercury forms two series of compounds, the mercurous and the mercuric compounds. In the mercurous compounds HgX it is apparently univalent but they probably have the doubled formulae Hg_2X_2 and contain the bivalent group $-Hg-Hg-$ in which mercury is bivalent. The mercuric compounds HgX_2 contain bivalent mercury $-Hg-$.

MERCUROUS COMPOUNDS

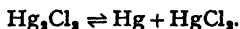
Mercurous fluoride Hg_2F_2 is a yellow crystalline solid, soluble in water, formed by dissolving mercurous carbonate in hydrofluoric acid.

Mercurous chloride Hg_2Cl_2 occurs native as *horn quicksilver*. It is formed by the action of chlorine on excess of mercury and is thrown down as a white precipitate on addition of hydrochloric acid or sodium chloride to mercurous nitrate solution. To obtain a pure product, excess of chloride is used and the solution heated.

Mercurous chloride is called *calomel* and is used in medicine as a purgative. It is prepared by subliming in an iron pot a mixture of mercuric chloride and metallic mercury, made by triturating the substances in a mortar; the crust of calomel formed on the lid of the pot is ground to powder and boiled with water to remove the very poisonous mercuric chloride, some of which always sublimes unchanged:



H. B. Baker found that the vapour density of calomel carefully dried over phosphorus pentoxide corresponds with the formula Hg_2Cl_2 . The vapour density of ordinary undried mercurous chloride apparently corresponds with the formula HgCl , but Harris and Victor Meyer in 1894 showed that the vapour is dissociated :



If the vapour is contained in a porous earthenware tube mercury diffuses out, whilst the residue in the tube contains an excess of HgCl_2 . Gold leaf introduced into the vapour is amalgamated by the free mercury. Salts of mercury do not react with gold.

Mercurous chloride is very sparingly soluble in water ; it dissolves to some extent in solutions of chlorides and in concentrated hydrochloric acid but is decomposed into mercuric chloride and mercury. Aqueous ammonia converts it into a black powder, formerly regarded as a definite compound Hg_2ClNH_2 , but probably consisting of a mixture of black finely divided mercury and the *mercuric* compound called "infusible white precipitate" (p. 362), viz. $\text{Hg} + \text{Hg}(\text{NH}_2)\text{Cl}$. A similar black precipitate of $\text{Hg} + \text{Hg}(\text{NH}_2)\text{NO}_3$ is thrown down when ammonia is added to mercurous nitrate solution.

Mercurous bromide Hg_2Br_2 is similar to calomel. The **iodide** Hg_2I_2 is formed as a green powder by triturating excess of mercury and iodine. On heating it becomes yellow. The pure iodide, formed by boiling excess of iodine with mercurous nitrate containing a little nitric acid and cooling, consists of transparent yellow crystals which blacken on exposure to light.

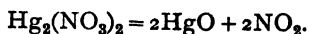
Mercurous oxide Hg_2O is formed as a black powder by triturating calomel with sodium hydroxide solution or by precipitating a solution of mercurous nitrate with sodium hydroxide. It readily decomposes on warming or on exposure to light into mercury and mercuric oxide, and is possibly only a mixture of mercuric oxide and finely divided mercury, as its X-ray diagram indicates.

Mercurous carbonate Hg_2CO_3 is precipitated as a yellow powder on adding excess of potassium bicarbonate to mercurous nitrate solution and allowing to stand for a few days to decompose any basic nitrate. It decomposes on exposure to light or when gently heated :



Mercurous nitrate $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is formed by the action of dilute nitric acid on excess of mercury in the cold, and readily crystallises from the solution on standing. If water is added to the crystals a white precipitate of a basic nitrate is produced, which redissolves in dilute nitric acid. A little mercury is usually kept in the solution to prevent oxidation to the

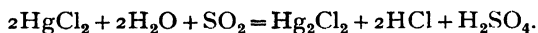
mercuric compound. Mercurous nitrate decomposes on heating into nitrogen dioxide and mercuric oxide :



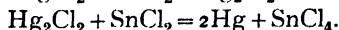
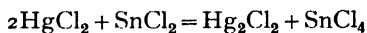
Mercurous sulphide does not seem to exist. **Mercurous sulphate** Hg_2SO_4 is formed by warming an excess of mercury with concentrated (or fuming) sulphuric acid and deposits as a coarse crystalline powder on cooling. It is formed as a white precipitate by adding sulphuric acid to a solution of mercurous nitrate. It tends to hydrolyse when washed and a basic salt is formed. According to Hulett (1904) the pure sulphate is best obtained by electrolysis with a mercury anode in dilute sulphuric acid. Mercurous sulphate is used as a depolariser in the Weston cell.

MERCURIC COMPOUNDS

The mercuric compounds HgX_2 are formed by the oxidation of mercurous compounds. Calomel dissolves in *aqua regia* forming mercuric chloride HgCl_2 . The mercuric compounds, conversely, may be reduced to mercurous compounds or to metallic mercury. Calomel is precipitated if sulphur dioxide is passed into a solution of mercuric chloride :



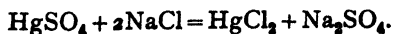
By the action of a solution of stannous chloride, white calomel or grey finely divided mercury is precipitated according to the amount added :



All compounds of mercury are reduced to the metal on boiling with hydrochloric acid and copper foil ; the foil becomes white owing to amalgamation, and on heating it in a glass tube a sublimate of minute globules of mercury is formed. A similar sublimate is obtained if a mercury salt is heated with powdered charcoal and sodium carbonate.

Mercuric fluoride HgF_2 is formed by heating mercurous fluoride in dry chlorine at 275° or alone in a vacuum at 450° ; it is discoloured by traces of moisture. The hydrate $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$ is formed in white crystals by dissolving mercuric oxide in excess of hydrofluoric acid, and is easily hydrolysed by water to a yellow basic salt $\text{HgF}(\text{OH})$.

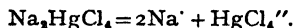
Mercuric chloride HgCl_2 , sometimes called *corrosive sublimate* on account of its volatility and poisonous properties, is formed at the ordinary temperature by the action of chlorine on mercury, even when the materials are very dry. It is made by heating mercury in chlorine, or by subliming a mixture of mercuric sulphate, common salt and a little manganese dioxide in a long-necked flat-bottomed flask heated in a sand-bath :



The manganese dioxide prevents the formation of calomel from some mercurous sulphate usually contained in the mercuric sulphate. The flask is broken after cooling and the cake of sublimate removed from the upper part.

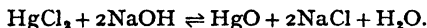
Mercuric chloride forms colourless needles, sparingly soluble in cold but readily in hot water. It is easily fusible and can be sublimed. It is a violent poison and is used for preserving skins in taxidermy, as a bactericide and in very dilute solution for sterilising instruments in surgery. It is readily soluble in alcohol and in ether (which extracts it from a solution in water). The aqueous solution is slightly hydrolysed and the salt is only slightly ionised. On account of its small ionisation, mercuric chloride is not decomposed by boiling concentrated sulphuric acid. It is not acted upon by nitric acid.

Mercuric chloride dissolves with evolution of heat in concentrated hydrochloric acid; the solution does not fume and on cooling deposits crystals of HHgCl_2 . With chlorides of alkali metals crystalline compounds are formed, e.g. KHgCl_2 and Na_2HgCl_4 , which are partly decomposed in solution and partly ionised into complex ions:



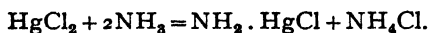
A solution of Na_2HgCl_4 is used instead of mercuric chloride as an antiseptic, since it is neutral in reaction and does not coagulate proteins. The ammonium salt $(\text{NH}_4)_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ is called *sal alembroth*.

Alkalis precipitate a solution of mercuric chloride only incompletely, and mercuric oxide dissolves in hot solutions of alkali chlorides forming strongly alkaline liquids:



This depends on the small ionisation of mercuric chloride, the concentration of mercuric ions from the dissociation of which is less than that in the very dilute saturated solution of mercuric oxide. The latter therefore dissolves with formation of un-ionised chloride.

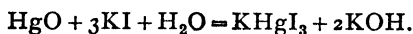
By the action of ammonia gas on solid mercuric chloride, or by precipitating a boiling solution of ammonium chloride and ammonia with mercuric chloride solution, a white solid called *fusible white precipitate* $\text{HgCl}_2 \cdot 2\text{NH}_3$ or $[\text{Hg}(\text{NH}_3)_2]\text{Cl}_2$ is formed. When ammonia solution is added to mercuric chloride solution, mercuric oxide is not obtained (as with caustic potash or soda) but *infusible white precipitate*, which is *amino-mercuric chloride* $\text{NH}_2 \cdot \text{HgCl}$, i.e. mercuric chloride in which one atom of chlorine is replaced by the amino-group NH_2 :



Mercuric bromide HgBr_2 is similar to the chloride and is formed from mercury and bromine or by dissolving mercuric oxide in hydrobromic acid.

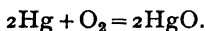
Mercuric iodide HgI_2 is formed as a yellow precipitate, which rapidly becomes scarlet, on adding the calculated amount of potassium iodide solution to mercuric chloride solution. On heating to 126° it is converted into another crystalline form which is yellow. The reverse change occurs on cooling, especially if the substance is rubbed. The yellow form is deposited on sublimation. The iodide is sparingly soluble in water but more soluble in alcohol. It is not decomposed by dilute alkalis.

Mercuric iodide readily dissolves in solutions of mercuric chloride or potassium iodide. In the second case a complex compound, **potassium mercuri-iodide** KHgI_3 is formed. The solution is not precipitated by bases since practically no mercuric ions are present, and mercuric oxide dissolves in a solution of potassium iodide to form a strongly alkaline liquid :

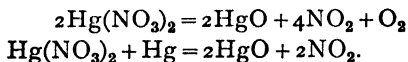


A solution of potassium mercuri-iodide containing excess of potassium hydroxide is used as a test for ammonia under the name of **Nessler's reagent**. With traces of ammonia a brown colour, with larger amounts a brown precipitate of $\text{NH}_2\text{Hg}_2\text{I}_3$, is formed.*

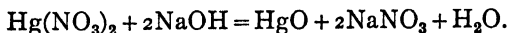
Mercuric oxide HgO is formed as a dense red crystalline powder (*mercurius praecipitatus per se*) by heating mercury for a long time just below its boiling point in a flask with a long neck open to the air :



The red crystalline oxide is also obtained (as "red precipitate") by heating mercuric nitrate or a mixture of mercuric nitrate and mercury (at higher temperatures the mercuric oxide decomposes) :



Sodium or potassium hydroxide (*not* ammonia) gives a yellow precipitate of the finely divided oxide from a solution of mercuric nitrate ; according to Ostwald this differs from the red oxide only by the particles being smaller :



By digesting mercuric oxide with warm aqueous ammonia a yellow powder known as *Millon's base* is obtained. This is now formulated as $\text{HO}(\text{Hg}_2\text{O})\text{NH}_2 \cdot \text{H}_2\text{O}$, since it loses water when dried in ammonia gas and forms $\text{HO} \cdot \text{Hg}_2\text{O} \cdot \text{Hg} \cdot \text{NH}_2$.

Mercuric carbonate is known only in the form of a brown basic salt $\text{HgCO}_3 \cdot 2\text{HgO}$ precipitated by potassium carbonate from mercuric nitrate solution.

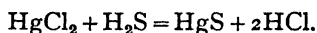
* This precipitate was previously given the formula $(\text{Hg}_2\text{O})\text{NH}_4\text{I}$ or $\text{NH}_4\text{I} \cdot \text{H}_2\text{O}$.

Mercuric cyanide $\text{Hg}(\text{CN})_2$, which is only slightly ionised, is formed by dissolving mercuric oxide in aqueous hydrocyanic acid and crystallising; it is used in the preparation of cyanogen. The **thiocyanate** $\text{Hg}(\text{CNS})_2$ is formed as a white precipitate on adding KCNS to $\text{Hg}(\text{NO}_3)_2$ solution; when made into small pills with gum tragacanth soaked in water and lit with a taper it gives poisonous fumes of mercury and a long, snake-like mass of a polymerised cyanogen product (*Pharaoh's serpent*).

Mercuric fulminate $\text{Hg}(\text{ONC})_2$ (isomeric with the cyanate) is obtained as a white precipitate on warming a solution of mercury in excess of nitric acid with alcohol. It is used in making detonators, since it explodes on percussion. It is being replaced to some extent by lead azide $\text{Pb}(\text{N}_3)_2$.

Mercuric nitrate is obtained in large very deliquescent colourless crystals $2\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ by boiling mercury with excess of concentrated nitric acid, cooling and evaporating over quicklime in a desiccator. Mercuric nitrate is decomposed by water and the basic salt $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgO} \cdot \text{H}_2\text{O}$ is formed as a white powder, decomposed into oxide by further action of water. Mercuric nitrate is precipitated from solution by concentrated nitric acid.

Mercuric sulphide HgS occurs native as *cinnabar* and is the pigment *vermilion*. It is formed by subliming mercury with sulphur or by triturating mercury and sulphur with a little alkali hydroxide solution, when the black sulphide first produced slowly becomes red and crystalline. The red form is less soluble in alkali sulphides than the black and hence the latter when digested with sodium sulphide solution is slowly converted into scarlet vermilion. Mercuric sulphide is formed by precipitating a solution of the chloride with hydrogen sulphide:



The black precipitate of HgS first formed becomes white if shaken with the excess of mercuric chloride solution, the compound $\text{HgCl}_2 \cdot 2\text{HgS}$ being produced. The further action of H_2S changes this into a red and finally a black precipitate (HgS). The black precipitate becomes red on sublimation. It is insoluble in boiling hydrochloric or dilute nitric acid, but dissolves in *aqua regia* or in concentrated solutions of potassium or sodium sulphides (forming thio-salts, e.g. K_2HgS_3).

Mercuric sulphate HgSO_4 is obtained by boiling mercury with concentrated sulphuric acid and evaporating to dryness:



The white residue may be crystallised from sulphuric acid. With a *small* quantity of water it forms colourless crystals of $\text{HgSO}_4 \cdot \text{H}_2\text{O}$, but it readily hydrolyses, producing a yellow crystalline powder $\text{HgSO}_4 \cdot 2\text{HgO}$, sparingly soluble in water and called *turpeth mineral*.

CHAPTER XXV

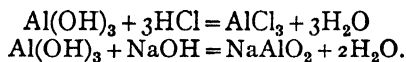
BORON AND ALUMINIUM

Group III in the periodic table is divided into two parts:

Sub-group (a): Rare-earth Metals.

Sub-group (b): Boron, Aluminium, Gallium, Indium and Thallium.

All these elements form oxides R_2O_3 and chlorides RCl_3 . They are generally trivalent. Boron forms some anomalous hydrides, thallium forms univalent compounds TlX which are more stable than the trivalent compounds TlX_3 , and some rare-earth elements form compounds MX_2 . Boron trioxide is weakly acidic, but shows feebly basic properties towards very strong acids. The basic character of the oxides increases with the atomic weight. The hydroxides of the (b) sub-group are amphoteric, forming salts both with strong acids and with strong bases:



The metals of the (b) sub-group do not oxidise very easily in the air, though this tendency increases with the atomic weight. Aluminium is fairly stable in the air, whilst thallium oxidises moderately easily. Aluminium, gallium and indium form characteristic alums with the formula $M_2SO_4 \cdot R_2(SO_4)_3 \cdot 24H_2O$, which are isomorphous, M being a univalent metal. A true thallic alum has not been prepared but thallic aluminium alum $Tl_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ is quite stable.

BORON

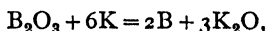
History.—Some boron compound, perhaps boric acid, was known in the Roman period since red pottery (*terra sigillata*) glazed with borate has been found. The Greek word *chrysokolla*, one meaning of which was a flux used in soldering gold, has been translated "borax" but it may have meant some copper compound. Borax, used as a flux, was brought from Tibet in the Middle Ages and was called *tincal*.

Boric acid was obtained by Homberg in 1702 by subliming borax with green vitriol ($FeSO_4 \cdot 7H_2O$), and the nature of the product (called *sal sedativum*) was explained in 1747 by Baron, who showed that it formed borax with soda. Lavoisier suggested that boric acid anhydride (B_2O_3) was the oxide of an unknown radical. Boron was first obtained as an olive-brown powder by Davy in 1807 by electrolysis of moist boric acid, and in 1808

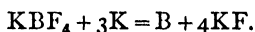
by heating fused boric oxide with potassium. The second method was used by Gay-Lussac and Thenard in 1808 to obtain boron in larger quantity.

Occurrence.—Boron occurs mainly as boric acid and borates (p. 370).

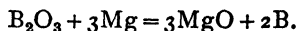
Preparation.—Boron is formed on heating boron trioxide with sodium or potassium :



or more easily by heating potassium fluoborate with potassium :



What is called *amorphous boron* is prepared by Moissan's process (1895) by heating a mixture of 1 part of magnesium powder and 3 parts of freshly fused and powdered boron trioxide in a covered porcelain (or better silica) crucible. A violent reaction occurs :



The cooled mass is heated with diluted hydrochloric acid (1 : 2) in a beaker and the dark-brown powder of boron is filtered, washed and dried in a steam oven. Amorphous boron is impure and contains oxygen and magnesium ; it may be purified to some extent by strongly heating in a vacuum.

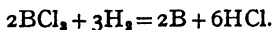
Amorphous boron is unaltered in air at ordinary temperatures but smoulders just below a red heat, boron oxide and nitride (BN) being formed which protect the boron by forming a coating over the particles. It burns brilliantly when heated in oxygen and chlorine, and reacts with fused alkalis evolving hydrogen and forming a borate :



It is not attacked by dilute acids but hot concentrated nitric and sulphuric acids oxidise it to boric acid. It displaces carbon from carbon dioxide and silicon from silica on heating.

Crystalline boron was obtained by Wöhler and Deville (1857) by fusing amorphous boron with aluminium ; on cooling crystals of boron separate and after dissolving the aluminium in acid these remain as "adamantine boron" in the form of diamonds, some clear and colourless and others brown. These are very hard and resistant to heat and acids but dissolve in fused alkalis. They are not pure boron but always contain aluminium.

Pure boron is obtained by striking an alternating current arc between water-cooled copper electrodes in a mixture of hydrogen and boron trichloride vapour in a glass globe. The boron powder collecting on the electrodes fuses to globules, which drop off :

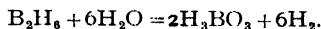


The boron so prepared is quite different in properties from amorphous boron. It is a black very hard infusible solid with a conchoidal fracture, which may be strongly heated in air without oxidation and is only slowly attacked by hot concentrated nitric acid.

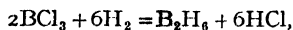
BORON COMPOUNDS

Several **boron hydrides** are present in the gas formed by the action of hydrochloric acid on magnesium boride, which is prepared (mixed with magnesium oxide) by heating equal weights of powdered boron trioxide and magnesium powder in a crucible. The gas is mostly free hydrogen but it has a peculiar smell and burns with a green-edged flame. The boron hydrides can be condensed out with liquid air and fractionated.

The main product is the hydride B_4H_{10} , which decomposes on warming into B_2H_6 and hydrogen. *The hydride BH_3 is not known.* B_2H_6 is a fairly stable gas but is decomposed by water:



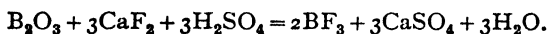
Other hydrides are B_6H_6 , and the solid $B_{10}H_{14}$. B_2H_6 is formed on passing an electric discharge through a mixture of BCl_3 or BBr_3 vapour and hydrogen under reduced pressure:



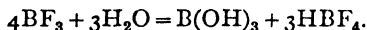
but is most easily prepared by the action of lithium aluminium hydride (see p. 382) on boron trichloride in dry ether:



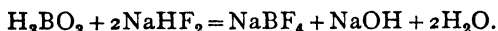
Boron fluoride BF_3 is obtained by the spontaneous combustion of boron in fluorine, by heating potassium fluoborate (KBF_4) with B_2O_3 , or by heating a mixture of fluorspar, boron trioxide and concentrated sulphuric acid:



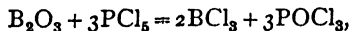
The gas is collected over mercury. It fumes strongly in moist air and when passed into water gives boric acid and hydrofluoboric acid:



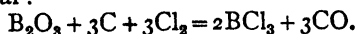
This acid forms salts called **fluoborates**, *e.g.* KBF_4 is thrown down as an amorphous white precipitate on addition of a potassium salt to the acid. Fluoborates are formed in solution from boric acid and acid fluorides:



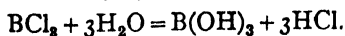
Boron chloride BCl_3 is obtained by heating amorphous boron in chlorine, by heating B_2O_3 with phosphorus pentachloride in a sealed tube:



or by passing dry chlorine over a strongly heated mixture of boron trioxide and charcoal:



It is condensed in a freezing mixture. The colourless liquid is freed from chlorine by distillation over mercury. It fumes strongly in moist air and is immediately and irreversibly hydrolysed by water:



Boron bromide BBr_3 is a colourless viscous liquid formed from the elements; the iodide BI_3 is a white crystalline solid formed by passing hydrogen iodide and boron chloride vapour through a heated tube.

Boron trioxide B_2O_3 is formed when amorphous boron burns in oxygen but is more conveniently prepared by heating boric acid, which loses water and finally the oxide fuses; on cooling a glassy mass of boron trioxide is formed:



Boron trioxide shows feebly basic as well as acidic properties and thus resembles alumina (p. 377). Boric acid combines with sulphur trioxide to form boron hydrogen sulphate $\text{B}(\text{HSO}_4)_3$, and with phosphoric acid to produce boron phosphate BPO_4 , insoluble in water and dilute acids but soluble in alkalis.

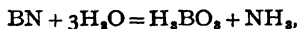
Boric acid.—Boric (or boracic) acid is prepared from borax by the action of a mineral acid. It is sparingly soluble in cold water but more readily in hot water.

To a hot saturated solution of borax concentrated hydrochloric acid is added till the solution is strongly acid to litmus. On cooling, scaly six-sided crystals of boric acid separate:



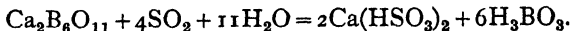
These are washed with cold water and recrystallised from hot water.

In the volcanic regions of Tuscany jets of steam called *soffioni* escape from the ground; these contain traces of boric acid, which is volatile in steam. The boric acid may have been produced by the action of superheated water on boron nitride:



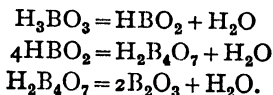
or on tourmaline, which contains 3-4 per cent. of B_2O_3 and is found *in situ*. In the recovery of the boric acid, a basin is built around two or three of the *soffioni*, and the steam is condensed in water. The liquid is concentrated in flat lead pans by the heat of the steam, and the crystals of boric acid separating are recrystallised and dried. In the modern process the steam is used to generate electric power and the boric acid is crystallised from the condensed water.

Most of the boric acid of commerce is made from native calcium borate (*colemanite*) $\text{Ca}_2\text{B}_6\text{O}_{11}$ found in California and South America: this is ground, suspended in boiling water and sulphur dioxide passed in, when a solution of calcium bisulphite is formed and crystals of boric acid separate on cooling:

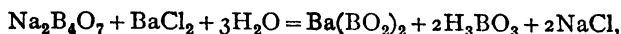


Ordinary boric acid, or **orthoboric acid** H_3BO_3 , forms soft silky pearly-white crystals with a greasy feel. On heating at 100° these lose water and form **metaboric acid** HBO_2 . At 140° **pyroboric acid** $\text{H}_2\text{B}_4\text{O}_7$ is said to be

formed ; at a high temperature boric anhydride or boron trioxide B_2O_3 is formed, which softens to a hygroscopic glassy mass at a red heat :



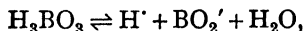
Orthoborates are uncommon, magnesium borate $Mg_3(BO_3)_2$ and ethyl borate $B(OC_2H_5)_3$ being best known. **Metaborates** are the most stable and pyroborates are also stable. Borax or sodium pyroborate $Na_2B_4O_7$, since it contains twice as much boric anhydride B_2O_3 as the metaborate is also called a diborate : $Na_2O, 2B_2O_3$. Metallic borates, usually metaborates, are precipitated by adding a solution of borax to solutions of the metallic salts :



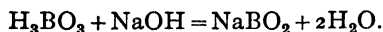
and are precipitated in Group III on adding ammonia if boric acid is present. Since this interferes with the group separation the boric acid is removed by repeated evaporation with dilute hydrochloric acid, as it is volatile in steam.

Boric acid turns litmus a wine-red colour but has no action on methyl orange. Turmeric paper dipped into a solution of the acid (or a borate) mixed with hydrochloric acid turns brownish-red on drying ; alkali changes this colour to greenish-black.

Boric acid is a very weak acid, weaker than carbonic acid or hydrogen sulphide. It ionises as a *monobasic acid* :



and may be titrated with alkali and phenolphthalein after addition of glycerol which increases the strength of the boric acid :



Borax may be titrated with acid and methyl orange as though it were a caustic alkali :



Boric acid is used as an antiseptic and in making glasses, glazes and enamels.

Ethyl borate $B(OC_2H_5)_3$ is formed by distilling a borate with alcohol and concentrated sulphuric acid. Its vapour burns with a beautiful green flame.

The mixture is heated in a flask fitted with a jet leading the vapour into a wider tube where it mixes with air ; the mixture of air and vapour is kindled and burns at the top of the tube (Fig. 158).

Borax.—The commonest borate is sodium pyroborate or *borax* $Na_2B_4O_7$, which is prepared by

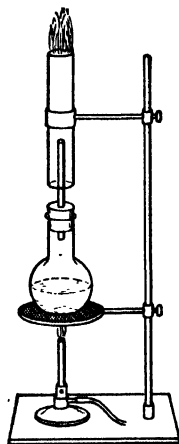
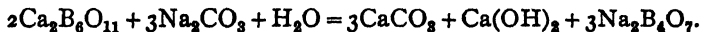


FIG. 158.—Green flame of ethyl borate.

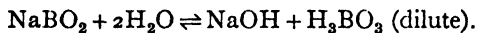
recrystallising the natural salt of Lake Borax or of Searle's Lake (California). It is also prepared by boiling the finely powdered calcium (or magnesium) borate minerals (*colemanite* $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ of Asia Minor and America; *boracite* $\text{MgCl}_2 \cdot 2\text{Mg}_3\text{B}_5\text{O}_{15}$ of Stassfurt; *boronatrocalcite* $\text{CaNaB}_6\text{O}_{10} \cdot 8\text{H}_2\text{O}$ of Chile) with sodium carbonate solution, filtering and crystallising:



Below 60° the borax crystallises with $10\text{H}_2\text{O}$ as common (monoclinic) borax; above 60° octahedral borax with $5\text{H}_2\text{O}$ separates. Crystalline borax on heating swells up and loses water and at a higher temperature the anhydrous borax fuses to a transparent glass which dissolves metallic oxides, often with characteristic colours ("borax beads"): blue (CuO , CoO), red (Cu_2O), green (Cr_2O_3 , FeO), brown (Fe_2O_3), yellowish-brown (NiO), violet (MnO); metaborates are formed:



Borax is hydrolysed in solution, which reacts alkaline, the metaborate being first formed*:



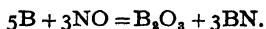
Borax is used in laundering for softening water and imparting a gloss to linen in ironing, in preparing glazes, as a flux in soldering, in making optical and hard glass, and (on account of the properties of boric acid) as an antiseptic.

Sodium perborate is obtained by the action of hydrogen peroxide and sodium hydroxide, or of sodium peroxide, on cooled borax solution. The compound is $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, but it was formerly supposed to be a borate containing hydrogen peroxide of crystallisation, $\text{NaBO}_3 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$. It does not liberate iodine from concentrated potassium iodide solution. The compound ("perborax") is stable when dry and only sparingly soluble in water. The solution has bleaching and antiseptic properties and is also stable at room temperature but evolves oxygen on warming.

Boron is one of the few elements which combine directly with nitrogen (p. 465); boron nitride BN is prepared by heating borax with ammonium chloride, extracting with hydrochloric acid and washing:



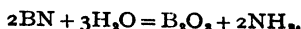
Boron burns when heated in nitric oxide:



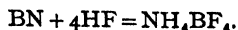
Boron nitride is a white infusible powder, unchanged by mineral acids,

* It should be noted that the ion $\text{B}_4\text{O}_7^{--}$ is not formed.

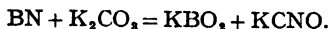
solutions of alkalis, or chlorine at a red heat. It is decomposed by fusion with potash and when heated in steam :



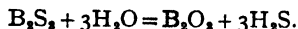
or (slowly) by hydrofluoric acid :



When fused with potassium carbonate, it forms potassium cyanate :



Boron forms a very hard carbide B_4C on heating the oxide with carbon in the electric furnace, and a sulphide B_2S_3 by direct combination at a white heat, or by heating B_2O_3 with carbon in the vapour of CS_2 . The sulphide is hydrolysed by water :



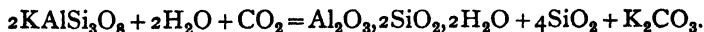
The atomic weight of boron has been found from the ratios $\text{BCl}_3 : 3\text{AgCl}$ and $\text{BBr}_3 : 3\text{AgBr}$, and by the analysis of gaseous boron hydride B_2H_6 . The valency follows from the vapour density of BCl_3 and of organic compounds ; the atomic heat is abnormal (p. 90).

ALUMINIUM

History.—Alum, from which the element aluminium takes its name, was known in very early times. Pott (1746) showed that it was derived from a peculiar earth, *alumina*, which Marggraf (1754) was first able to isolate from clay. That alumina was the oxide of a metal was proved by Davy, who isolated the impure metal which he called *aluminum*. A purer metal was obtained by Oersted (1824) by heating the amalgam obtained by the action of potassium amalgam on aluminium chloride. The pure metal was first obtained by Wöhler in 1827 by the action of potassium on the chloride AlCl_3 . Bunsen (1854) prepared it by electrolysis but the first industrial method of preparation, due to Deville (1854), depended on the reduction of sodium aluminium chloride NaAlCl_4 by sodium. In 1886 the production of aluminium by the electrolysis of alumina dissolved in fused cryolite was started simultaneously by Héroult in France and Hall in America.

Occurrence.—Aluminium occurs in almost all *silicate rocks* (felspar, augite, hornblende, chlorite, tourmaline and micas) and in the secondary formations *clay* ($\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$) and *slate* (clay hardened and laminated by pressure). The oxide Al_2O_3 is found either anhydrous as *corundum*, or hydrated as *diaspore* $\text{Al}_2\text{O}_3, \text{H}_2\text{O}$, *gibbsite* $\text{Al}_2\text{O}_3, 3\text{H}_2\text{O}$ and *bauxite*, a mixture of diaspore and gibbsite in varying proportions. *Spinel* is MgAl_2O_4 . *Felspar* KAlSi_3O_8 or $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$ is a constituent of primary rocks such as granite, and by their disintegration by the combined action of moisture and atmospheric carbon dioxide

soluble alkali salts and insoluble hydrated aluminium silicate (clay) are formed :



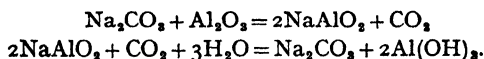
The quartz crystals and mica scales remain with the fine deposit of clay or *kaolin*, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Any iron in the rock is oxidised to ferric oxide, which colours the clay yellow or red. The kaolin may be separated from the quartz by washing, when the fine particles of clay are carried away from the larger pieces of quartz. A pure clay which has been transported by water and is more plastic than kaolin or china clay is called *ball clay*.

Common clay is contaminated with limestone, quartz and oxide of iron ; a mixture of clay and limestone is *marl*, a mixture of clay and sand is *loam*. Aluminium compounds are not absorbed (except in traces) from soils by plants with the exception of mosses, the ash of which is rich in alumina.

Cryolite Na_3AlF_6 is a semi-transparent mineral found only in Greenland.

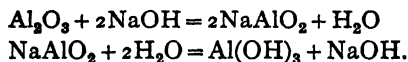
Metallurgy of aluminium.—It is not practicable to produce aluminium from clay ; the source of the metal is *bauxite*, but since this contains iron oxide and silica it is first purified to obtain pure alumina.

In the old process bauxite is heated to redness with sodium carbonate, when sodium aluminate NaAlO_2 is produced, alumina being a feebly acidic oxide. The mass is treated with water, forming finely divided oxide of iron which can be used for the purification of coal gas (p. 407) and a solution of sodium aluminate, from which a granular precipitate of aluminium hydroxide is thrown down by carbon dioxide :



On igniting the precipitate, Al_2O_3 is obtained and the solution of Na_2CO_3 is evaporated and used again.

The British Aluminium Co. at Larne (Ireland) uses the *Bayer process*. The calcined bauxite is digested with sodium hydroxide solution under pressure, giving a solution of sodium aluminate and leaving oxide of iron which cannot be used for any purpose. The solution of sodium aluminate (with some sodium silicate) is agitated with precipitated alumina, when nearly all the aluminium in solution is thrown out as a sandy precipitate of hydroxide (β -alumina), which is easily washed and on calcination yields pure alumina :



The alumina is then dissolved in fused cryolite (now usually artificial) and electrolysed with carbon electrodes.

The electric furnace consists of an iron box lined with blocks of carbon and made the cathode. The anodes are carbon rods set in a row (Fig. 159) about 2 to 3 in. above the bottom of the trough. The temperature is over 900° .

The alumina is electrolysed; the liquid aluminium forms a pool below the anodes and the oxygen liberated burns the anodes to CO and CO_2 in about equal volumes. The charge is covered with solid alumina and fresh alumina is added from time to time to replace that decomposed. The decomposition is indicated by a rise in resistance, the shunted lamp brightening. The metal has a purity of 99 per cent. Al, the impurities being chiefly iron and silicon.

Pure aluminium (99.98 per cent.) is made by the *Hoopes' process*. A liquid aluminium-copper alloy anode is covered with fused cryolite and barium fluoride, floating on which is a cathode of pure molten aluminium. The very pure metal differs in many properties from the 99 per cent. metal.

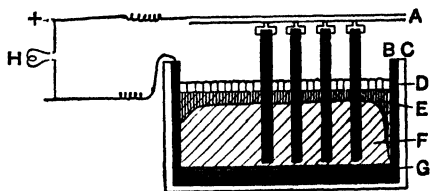


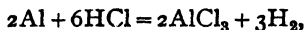
FIG. 159.—Electric furnace for aluminium: A. carbon anodes; B. carbon lining; C. cast-iron vessel; D. solid alumina; E. crust of solidified electrolyte; F. molten electrolyte; G. molten metal; H. low voltage charge control lamp.

Properties.—Aluminium is a white metal with a blue tinge, very ductile and malleable. On account of its small density it is used in the construction of airships and parts of motor-cars; it has a high tensile strength. The alloy of aluminium and magnesium called *magnalium* is still lighter and can be worked easily in a lathe, whilst *duralumin*, an alloy of aluminium, copper, magnesium and manganese, can be worked hot or cold and hardened by quenching in water, the hardness being increased by tempering after quenching. Alloys of aluminium with copper are called *aluminium bronzes*.

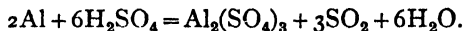
Aluminium is unaltered in dry air, a thin transparent protecting film of oxide being formed. This film is removed by rubbing the metal with moist mercuric chloride, producing a liquid amalgam to which the oxide cannot adhere, when rapid oxidation with production of moss-like excrescences of oxide occurs. Amalgamated aluminium foil is a useful reducing agent in neutral solutions. Aluminium foil or powder readily burns with a brilliant flame when heated in air. The metal is a good conductor of heat and electricity, being used for electric cables; for equal *weights* it is a better conductor than copper. The *powder* is made by stamping pieces of thin sheet in oil and really consists of thin flakes.

Although it is only superficially attacked by pure water, aluminium is attacked by sea water. Dilute or cold concentrated sulphuric acid

has very little action and the *pure* metal is almost unattacked by dilute or concentrated nitric acid. Dilute and concentrated hydrochloric acid readily dissolves it with evolution of hydrogen :



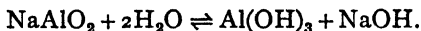
and hot concentrated sulphuric acid attacks it :



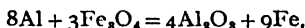
Aluminium readily dissolves in solutions of alkalis, forming **aluminates** :



These are hydrolysed in solution :



The great evolution of heat in the combination of aluminium with oxygen is utilised in Goldschmidt's *Thermit process* for reducing metallic oxides (*e.g.* Cr_2O_3 , Mn_2O_3) and for the production of molten iron for welding broken articles (rails, ship's parts, etc.) *in situ*. A mixture of aluminium powder and oxide of iron ("smithy scales") is placed in a crucible and ignited by a magnesium wire. A violent reaction occurs :



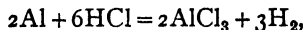
and molten iron covered with a layer of molten alumina is formed. The iron is tapped from below directly on to the joint to be welded, enclosed in a mould of fire-clay and sand.

ALUMINIUM COMPOUNDS

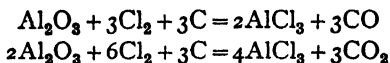
Halogen compounds.—Compounds of aluminium with all the halogens are known.

Aluminium fluoride AlF_3 is insoluble in water although aluminium dissolves in hydrofluoric acid; the salt is obtained in crystals by evaporating the solution. It is not decomposed by alkali solutions but only on fusion with sodium carbonate. The mineral *cryolite* is Na_3AlF_6 .

Anhydrous aluminium chloride AlCl_3 is prepared by heating aluminium in chlorine or hydrogen chloride gas :



by heating a mixture of alumina and carbon in a current of dry chlorine :



and by heating alumina in a stream of sulphur chloride vapour and chlorine :



In the laboratory, 10 gm. of aluminium turnings are heated in a hard glass tube connected with a bottle (Fig. 160) and a rapid current of chlorine dried by sulphuric acid is passed over the metal. A sublimate of aluminium chloride is formed.

Crude aluminium chloride is now largely used in petroleum "cracking" and is made from bauxite, carbon and chlorine.

Anhydrous aluminium chloride is a white crystalline very hygroscopic substance (usually coloured yellow by ferric chloride as impurity), which fumes in moist air and on heating easily sublimes without previous fusion. The vapour density at 350° corresponds approximately with Al_2Cl_6 but rapidly diminishes with rise of temperature until at 750° it corresponds with AlCl_3 , remaining constant at higher temperatures: $\text{Al}_2\text{Cl}_6 \rightleftharpoons 2\text{AlCl}_3$.

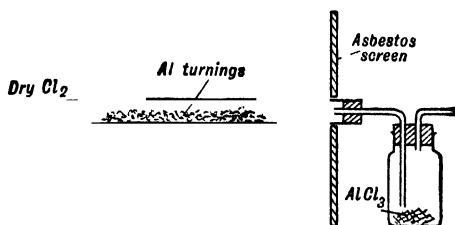
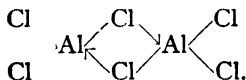


FIG. 160.—Preparation of aluminium chloride.

In organic solvents the formula is AlCl_3 . Its ready volatility and solubility in organic solvents indicate that aluminium chloride in some ways resembles a non-polar compound (*e.g.* BCl_3) rather than a salt. The solid is a moderate conductor of electricity but the melt a very poor one.

The structure of Al_2Cl_6 has been represented as:

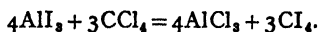


With a little water aluminium chloride forms a crystalline hydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, more conveniently prepared by dissolving aluminium or soluble alumina in concentrated hydrochloric acid and saturating the solution with hydrogen chloride gas. It is hydrolysed in solution: $\text{AlCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3 + 3\text{HCl}$, which can be titrated with alkali as if it were free hydrochloric acid. The compound NaAlCl_4 is formed when aluminium chloride and sodium chloride are heated in a sealed tube.

Aluminium bromide AlBr_3 is prepared similarly to the chloride and has similar properties.

Aluminium iodide AlI_3 is formed by heating aluminium and iodine in a sealed tube, or by acting on aluminium with iodine dissolved in carbon

disulphide. Aluminium iodide when heated with carbon tetrachloride forms carbon tetraiodide :



The bromide and iodide form crystalline hydrates with $6\text{H}_2\text{O}$.

Aluminium oxide.—Aluminium oxide or *alumina* Al_2O_3 occurs native as *corundum* in crystals nearly as hard as diamond; *emery* is an impure fine-grained variety used in grinding and polishing. Corundum when transparent forms a number of gems : *oriental topaz* (yellow), *sapphire* (blue, due to cobalt or titanium oxides), *ruby* (red, due to chromium oxide), *oriental amethyst* (violet, due to manganese oxide), *oriental emerald* (green). (The true emerald is beryllium aluminium silicate.)

Artificial rubies are produced by dropping powdered alumina containing chromium sesquioxide through the centre of an oxyhydrogen flame. The fused mass ("boule") is caught on a rod of alumina; it is not amorphous but forms a single crystal which may be cut. *Artificial sapphires* are made with alumina to which Fe_2O_3 and TiO_2 are added and a reducing flame is used.

Alundum, used as a refractory, is prepared by fusing bauxite in the electric arc furnace, allowing the impurities to settle, cooling, and crushing the upper part. The powder is mixed with a little clay and felspar, moulded, dried and fired in a porcelain kiln. It differs from silica in being a *basic* refractory.

Bauxite cement (*ciment fondu*) is made by fusing nearly equal weights of bauxite and lime. The clinker is finely ground. This cement, unlike ordinary cement, resists the action of sea water.

Aluminium hydroxide.—On adding an alkali to a solution of an aluminium salt, *e.g.* alum, a white gelatinous precipitate of **aluminium hydroxide** is produced, soluble in excess of alkali hydroxide (forming aluminates) but almost insoluble in dilute ammonia.

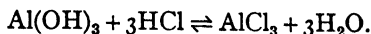
On heating the hydroxide to dull redness it loses water and forms a white powder of alumina. This is also formed by heating ammonia alum (p. 381). If it has not been strongly heated the alumina is soluble in acids, but when ignited it becomes insoluble in acids and can be brought into solution only by fusing with sodium hydroxide (forming sodium aluminate) or potassium hydrogen sulphate (forming aluminium sulphate). Some other oxides (*e.g.* chromium oxide, ferric oxide) behave similarly.

Precipitated aluminium hydroxide readily adsorbs colours and colloidal substances. Hence alum and aluminium salts are largely used as *mordants* in dyeing and for clarifying water and liquids such as sewage. In mordanting the alumina is first precipitated in the fabric and the latter

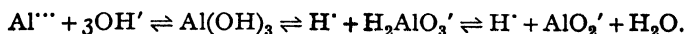
dipped into the solution of the dye. In clarification lime-water is added to precipitate alumina. Fabrics are waterproofed by steeping in a solution of aluminium acetate and steaming, when colloidal alumina is precipitated in the pores.

A colloidal solution of alumina is obtained by dialysing a solution of aluminium hydroxide in aluminium chloride solution (*cf.* ferric hydroxide, p. 610).

Aluminium hydroxide dissolves in acids producing aluminium salts :

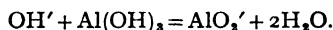


The reaction is reversible and the salts are hydrolysed by water, since aluminium hydroxide is a weak base. The hydroxide also dissolves in solutions of sodium or potassium hydroxides producing aluminates, which are extensively hydrolysed ; it is therefore capable of acting also as a weak acid. The acidic properties are weaker than the basic ; they are caused by the hydroxyl groups liberating hydrogen ions :



A substance having both acidic and basic functions in presence of strong bases and strong acids, respectively, is called an **amphoteric electrolyte** (or **ampholyte**). Its salts with strong acids and strong bases are hydrolysed in solution.

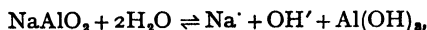
In solution, only the **meta-aluminates**, *e.g.* NaAlO_2 , appear to exist, since the freezing point of a solution of sodium hydroxide is unaltered by dissolved alumina, so that an OH' ion is replaced by AlO_2' :



If solutions of alumina in acid and alkali, respectively, are mixed, the whole of the alumina may be precipitated :



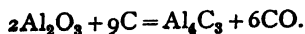
Solutions of aluminates are so largely hydrolysed :



that they may be titrated with acids as if they were caustic alkalis, and on standing the alumina is slowly deposited. When 'boiled with alumina, most of the aluminium hydroxide is precipitated.

The mineral *spinel* is $\text{MgO} \cdot \text{Al}_2\text{O}_3$ or MgAl_2O_4 and there are similar compounds in which Mg is replaced by Zn, Fe^{II} , Co^{II} and Mn^{II} . The cobalt compound CoAl_2O_4 , called *Thenard's blue*, is formed in the blowpipe test for aluminium (p. 617).

Aluminium carbide Al_4C_3 is a yellow solid formed by heating a mixture of alumina and carbon in the electric furnace :



With water or dilute acids it evolves methane (p. 397). Aluminium carbonate does not exist, since alumina is a very weak base.

Aluminium silicates and ceramics.—Aluminium silicates are found in many minerals and in clay, used for making ceramic products (Greek, *keramos*, clay, or a pot) such as bricks, pottery and porcelain.* Pure clay (*kaolinite*) $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ or $[\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2]_2 \cdot 3\text{H}_2\text{O}$, on heating loses free and combined water and shrinks; above 1000° reaction occurs with formation of cristobalite (p. 442) and *mullite* $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; at 1500° this sinters to a stony mass which at higher temperatures softens and then fuses.

Clay used in making pottery is washed and the coarse particles allowed to settle. The fine clay deposit is mixed with ground flint or felspar and excess of water is removed by air drying. It is then highly plastic and can be worked on the wheel. The goods are air dried by stacking in warmed rooms and then fired in clay boxes called *saggars*, stacked in a kiln. The product, which has undergone shrinkage, is called *biscuit*.

The plasticity of a clay depends on the state of hydration, fineness of the particles and content of organic matter; on baking a plastic clay tends to shrink and crack, so that some non-shrinking material such as calcined clay, bone ash, or ground flint is added to prevent this. For coarse earthenware, clay only is used.

Bricks are made from impure clay containing sand and oxide of iron, which gives them a red colour after firing at about 950° . The yellow bricks used in the South of England are made from mixtures of clay and chalk.

Sand-lime bricks are not made from clay but from a mixture of sand and slaked lime made to a paste with water, moulded and heated in steam at 125 lb. pressure; calcium silicate CaSiO_3 is formed and cements the sand particles together. Refractory *silica bricks* are made from crushed quartz or ganister (silica rock) bonded with 2 per cent. of lime (see p. 443).

Purer clay is used for *earthenware* which is fired at a higher temperature than bricks: the presence of ferric oxide produces a buff-coloured or red product. *Porcelain* is made from a mixture of the purest china-clay or *kaolin* free from iron, with ground felspar and quartz. It is fired at about 900° , then the glaze is put on and the goods are fired at a bluish-white heat (1300° – 1500°). The temperature is regulated by pyrometers, or by small clay cones (*Seeger cones*) which soften and bend over at particular temperatures in the furnace. The mass undergoes partial fusion and the product is translucent. *English bone china* contains 30 to 50 per cent. of bone-ash (calcium phosphate).

* Bourry and Searle, *A Treatise on Ceramic Industries*, 4th edit., 1926; Audley, *Silica and the Silicates*, 1921.

Clay containing much silica and alumina in comparison with basic oxides (Na_2O , CaO) is very refractory, and is called *fireclay* (e.g. Stourbridge clay). This is made into crucibles and refractory bricks and to prevent undue contraction on firing broken firebricks ("grog") are added to the clay before heating.

The clay after firing forms the *body*, *biscuit* if porcelain clay is used, otherwise *earthenware*. The *glaze* is a glassy surface imparted to the body and intimately united with it. Earthenware drain pipes and cheaper goods are *salt-glazed*; common salt is thrown into the kiln and vaporises at the high temperature, forming a thin layer of fusible silicate on the surface of the ware. Salt-glazed ware is suitable for containing acids. Table-ware is usually glazed by dipping it into a creamy paste of a mixture of borax, clay and ground flint. Some of this adheres to the surface and is fused in the furnace to a glass. *Porcelain glaze* is applied by dipping and re-firing at a lower temperature than in making the biscuit; the glaze may be ground felspar, quartz and kaolin. In making cheaper earthenware the glaze is put on before firing.

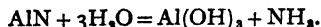
The ware may be *painted* before glazing or some colours are applied on the glaze; the colours are metallic oxides (e.g. cobalt oxide) which form coloured glasses with the glaze or with lead oxide and silica, or borax, mixed with the colouring oxide.

The blue mineral *lapis lazuli* is a sodium aluminium silicate containing sulphur in some form not completely defined but probably as sodium sulphide. In 1826 Guimet obtained artificial *lapis lazuli*, or *ultramarine*.

A mixture of kaolin, soda-ash or sodium sulphate, sulphur, and resin or wood charcoal is heated to redness in a closed crucible. A white ultramarine is formed in complete absence of air, but usually when air is admitted during heating a green ultramarine is formed. If this or white ultramarine is mixed with powdered sulphur and heated in air, the commercial blue ultramarine is formed, which is ground and washed. If this is heated in a stream of dry chlorine, nitric oxide, or hydrogen chloride, a violet and finally a red ultramarine result.

Alkalis are without action on ultramarine, so that it can be used in laundering to give a white appearance to linen, as it is not attacked by soap or soda. Acids, however, rapidly decompose it forming hydrogen sulphide and a white gelatinous residue.

Aluminium nitride AlN is formed by heating aluminium in nitrogen; it is decomposed by hot dilute alkali:



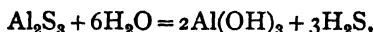
The formation and decomposition of aluminium nitride was proposed by Serpek for the utilisation of atmospheric nitrogen but the process does not seem to be used.

Aluminium nitrate $\text{Al}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ is a deliquescent salt prepared by dissolving the precipitated hydroxide in dilute nitric acid, evaporating and crystallising. It decomposes on heating, alumina being formed.

Aluminium phosphide AIP is formed by heating aluminium powder and red phosphorus; it is decomposed by water with evolution of phosphine.

Aluminium phosphate AlPO_4 is precipitated by adding a neutral solution of an aluminium salt to sodium phosphate solution; it is soluble in mineral acids, alkalis and ammonia. A basic aluminium phosphate coloured by copper is the true *turquoise*.

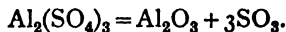
Aluminium sulphide Al_2S_3 is formed by heating aluminium with sulphur or by passing carbon disulphide vapour over strongly heated alumina. It is completely hydrolysed by water :



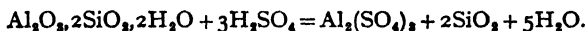
and only aluminium hydroxide is precipitated when ammonium sulphide is added to a solution of an aluminium salt.

Aluminium sulphate.—Aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$ occurs native as *hair salt* or *feather alum*; $\text{Al}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ is *websterite*.

If alumina is dissolved in hot concentrated sulphuric acid, the liquid on cooling slowly deposits an indistinctly crystalline mass of hydrated aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. This is purified by redissolving in a little water and adding alcohol, when an oily supersaturated solution separates, which soon solidifies to lustrous scaly crystals of the above formula. On heating, the crystals intumesce and lose water leaving a white mass of anhydrous sulphate, which decomposes when strongly heated :



Impure aluminium sulphate is made by heating kaolin (clay) with concentrated sulphuric acid, or bauxite with diluted sulphuric acid. In the first case silica separates :



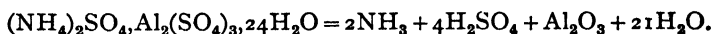
The settled solution is evaporated and the crystals pressed. The product may contain a considerable amount of ferric sulphate (especially if bauxite is used) which, although it does not form mixed crystals with aluminium sulphate, cannot be separated from it by crystallisation. The crude mixture, known as *alumino-ferric*, is used for the precipitation of colloidal matter from sewage. If the ferric is reduced to a ferrous salt, say by hydrogen sulphide, the aluminium sulphate may be crystallised out alone.

Alums.—The double salts of aluminium sulphate and potassium and ammonium sulphates are common *potash alum* $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or $KAl(SO_4)_2 \cdot 12H_2O$, and *ammonia alum* $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or $(NH_4)Al(SO_4)_2 \cdot 12H_2O$, respectively. They readily crystallise in octahedra (aluminium sulphate does not easily crystallise). Alum is prepared from *alum shale*, i.e. aluminium silicate permeated by pyrites FeS_2 , which on roasting in heaps forms aluminium sulphate. The roasted shale is lixiviated (or, if necessary, boiled with sulphuric acid) and after evaporation either ammonium or potassium sulphate or chloride is added, when alum is deposited. Potash alum is prepared from *alunite* or *alum-stone* $K_2SO_4 \cdot 3Al_2SO_4(OH)_4$, by roasting with fuel, exposing to air, lixiviating and crystallising :

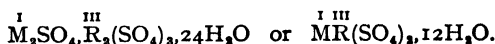


Alum is also made by adding an alkali sulphate to a solution of aluminoferric. Since alum is readily purified by recrystallisation it may be obtained free from iron (which gives dull colours to lakes in mordanting) much more readily than aluminium sulphate. Alum prepared from alunite, called *Roman alum*, although it is pink from the presence of ferric oxide, is quite free from soluble iron.

Potash alum when heated melts and loses the whole of its water at 200° , forming a white porous mass of *burnt alum*. Above a red heat the aluminium sulphate decomposes. Ammonia alum melts on heating, loses ammonia and sulphuric acid and on ignition leaves a residue of pure alumina :

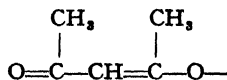


The name alum is given to all double-salts of the type

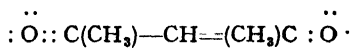


M may be Li, Na, K, NH_4 , Rb, Cs, (Ag ?), Tl , hydroxylaminium (NH_4O), or the radical of a quaternary nitrogen base, such as $N(CH_3)_4$. R may be Al, Fe, Cr, Mn, Ir, Ga, V, Co, Rh. Rare-earths do not form alums. The selenate radical SeO_4 may replace SO_4 . The alums are not stable complex compounds, since in solution they give the ions of the component salts. All the alums are isomorphous, form mixed crystals in all proportions and also layer-crystals, i.e. a crystal of any one alum continues to grow in a solution of any other. The sodium alum is very soluble and its preparation is difficult ; rubidium and caesium alums are sparingly soluble.

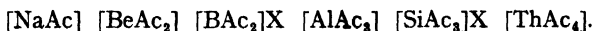
An interesting compound is aluminium acetylacetonate $AlAc_3$, where Ac is the radical of the enolic form of acetylacetonone $(CH_3CO)CH_2 \cdot CO \cdot CH_3$, viz.:



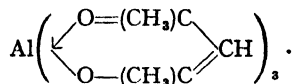
the electronic arrangements around the oxygens of which are:



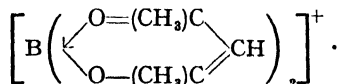
This is attached to the aluminium atom by one covalent bond and one co-ordinate linkage (see pp. 264 and 264B). Aluminium acetylacetonate is a neutral volatile compound with the normal vapour density. Similar compounds are formed with other elements but some of these are salts:



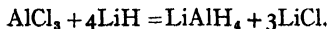
The aluminium atom has three valency electrons and shares these with the electrons on three right-hand oxygen atoms shown, to form three single covalent bonds. The three left-hand oxygen atoms form three co-ordinate links by donating three pairs of electrons to the aluminium atom, which is therefore surrounded by 12 shared electrons (6 covalencies):



In the case of boron, two molecules of acetylacetonate radical are linked to the boron atom, giving $2 + 4 = 6$ electrons. The boron has 3 electrons, and these would make a shell of 9 electrons. The stable shell for an element of the second period is 8, hence 1 electron is lost, and a positive ion is formed:



Lithium aluminium hydride, LiAlH_4 , is formed by the action of lithium hydride on aluminium chloride in dry ether:



It is a white solid, soluble in ether, stable in dry air but decomposed by water with evolution of hydrogen:



Lithium aluminium hydride is a good reducing agent.

The **atomic weight of aluminium** has been found from the ratio $\text{AlBr}_3 : 3\text{AgBr}$. The valency has been found from the atomic heat of aluminium and the vapour density of aluminium chloride above 750° , the vapour density of aluminium acetylacetonate and the molecular weight of AlCl_3 in solution in pyridine.

CHAPTER XXVI

CARBON

Group IV of the Periodic System contains :

Sub-group a : titanium, zirconium, hafnium, thorium.

Sub-group b : carbon, silicon, germanium, tin, lead.

Two elements (carbon and silicon) are non-metals and of the metals only two (tin and lead) are common.

In Group IV the differences between the odd and even series are ill-defined and the electrochemical characters of the elements are not very pronounced, because the group forms the transition between the electro-positive (base-forming) elements of Group III such as aluminium, and the electronegative (acid-forming) elements of Group V such as nitrogen and phosphorus.

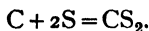
The two non-metals of the group have high melting points and in some forms show semi-metallic properties ; the metals, with the exception of tin and lead, also have high melting points. Carbon, silicon, germanium, tin, zirconium and thorium form hydrides RH_4 , and a gaseous hydride of lead has been described. All the elements form chlorides RCl_4 , although in the case of lead the stable chloride is $PbCl_2$ and both $SnCl_2$ and $SnCl_4$ are stable. The higher metallic chlorides, *e.g.* $SnCl_4$, are more like the chlorides of non-metals, *e.g.* $SiCl_4$, than salts. Carbon, silicon and germanium form the compounds $RHCl_3$ known as *chloroforms* (ordinary chloroform is $CHCl_3$).

The typical oxides RO_2 are all known, but many oxides and other compounds besides those corresponding with the type RX_4 are formed. In the cases of C, Si, Ge, Ti, Zr and Th the stable type is RX_4 ; Sn and Pb form stable compounds of the type RX_2 ; in the case of lead the only *stable* compounds of the quadrivalent type are the dioxide PbO_2 and some complex compounds. In many of its chemical properties lead shows close analogies to barium in the second group ; *e.g.* its sulphate $PbSO_4$ is very sparingly soluble in water and is isomorphous with $BaSO_4$, with which it often occurs native.

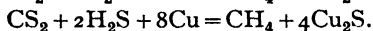
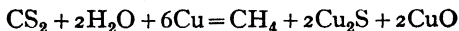
CARBON

The chemistry of carbon.—More than 600,000 carbon compounds have been described and the number is constantly increasing. The study of these compounds forms a special branch of chemistry which is still called “organic chemistry”, because living plants and animals are largely composed of carbon compounds and it was once supposed that these could be formed only by the agency of the “vital force”. This artificial barrier was broken down when it was shown, from early in the nineteenth century, that many carbon compounds occurring in plants and animals can be *synthesised*, *i.e.* prepared from their elements.

Carbon disulphide is easily formed from the elements on heating :

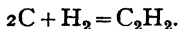


A mixture of carbon disulphide vapour with steam or hydrogen sulphide when passed over red-hot copper turnings forms methane CH_4 :

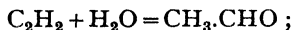


From methane, methyl alcohol and other “organic” compounds are easily prepared.

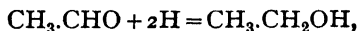
By burning an electric arc between carbon poles in hydrogen, acetylene is formed :



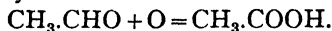
This can be made to add on water to form acetaldehyde :



from this by reduction alcohol is formed :



whilst by oxidation it yields acetic acid :



From alcohol and acetic acid numerous derivatives can be formed, and in this way an ever lengthening chain of carbon compounds may be built up from the elements.

Allotropic forms of carbon.—Carbon exists in two well-defined crystalline forms :

(1) **Diamond** (density 3.52).

(2) **Graphite** (*plumbago* or *black-lead*) (density 2.25).

There are several apparently amorphous varieties (but see p. 388) which may be grouped together as :

(3) **Charcoal** (varying density, from 1.3).

Diamond and graphite occur as minerals and anthracite coal is a mineral form of amorphous carbon. Compounds of carbon and hydrogen, called **hydrocarbons**, are very numerous and mixtures of them are

found in petroleum and in bituminous coal (which also contains some oxygen and nitrogen). Carbon dioxide CO_2 occurs both uncombined in the atmosphere and in combination as carbonates, such as calcium carbonate CaCO_3 (*chalk, limestone, and marble*), magnesium carbonate MgCO_3 , and a compound of calcium and magnesium carbonates called *dolomite* $\text{CaCO}_3, \text{MgCO}_3$.

That diamond, graphite and pure charcoal are all forms of the same element carbon is proved (i) by showing that equal weights of the three when burnt in oxygen give equal weights of the same product, carbon dioxide: $\text{C} + \text{O}_2 = \text{CO}_2$; (ii) by converting each form into the others.

Newton in 1704 from the similarity of its refractive index to those of oil of turpentine, camphor and amber, suggested that diamond might be "an unctuous [oily] substance coagulated". The same might have been said of flint glass. The Florentine Academicians in 1694 had heated a diamond in the focus of a powerful burning-glass and found that it glowed like a red-hot coal and disappeared, but D'Arcet in 1766 found that a diamond when strongly heated in a *closed* crucible remained unchanged. Davy and Faraday in 1814, using the original Florentine lens, burnt a diamond in oxygen. It took fire and continued to burn even if removed from the focus, with a steady brilliant light. Nothing was produced but carbon dioxide, which rendered lime-water milky. Smithson Tennant in 1797 burnt diamonds by strongly heating them with fused nitre in a gold tube and found that as much carbon dioxide was formed as Lavoisier had obtained from an equal weight of charcoal.

Clement and Desormes in 1802 showed that graphite when burnt in oxygen gives almost the same weight of carbon dioxide as an equal weight of pure charcoal, and Brodie in 1855 obtained pure graphite and showed that it was pure carbon.

The combustion of diamond in oxygen may be shown by strongly heating a splinter of *carbonado* (black diamond) by an electric current in a spiral of fine platinum wire supported by copper leads inside a jar of oxygen (Fig. 161). A little lime-water afterwards shaken with the gas is turned milky.

Diamond.—Marsden in 1881 heated charcoal with fused silver or an alloy of silver and platinum, dissolved the metal in nitric acid and obtained a very minute amount of black and also transparent crystals which were probably diamonds. Artificial diamonds were

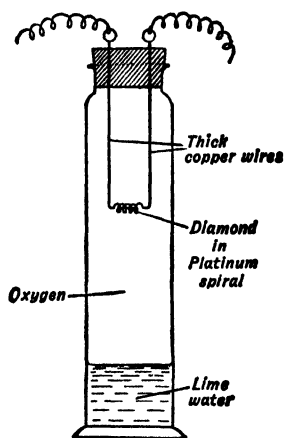


FIG. 161.—Combustion of diamond in oxygen.

prepared by Moissan in 1893. He heated charcoal with iron in the electric furnace to a very high temperature. Fused iron dissolves carbon and on cooling the iron slowly at atmospheric pressure most of the carbon deposits as graphite; when the iron is rapidly cooled under ordinary conditions the carbon remains in solid solution as the carbide Fe_3C . Moissan suddenly cooled the white-hot molten iron containing carbon by plunging the crucible taken from the electric furnace into cold water. On dissolving the iron from the solid with hydrochloric acid, a residue was left containing some microscopic diamonds (the largest 0.7 mm.), mostly black but some transparent.

These experiments were successfully repeated by Ruff in 1917; he found that diamonds were formed only when Moissan's experimental details were closely followed and not by other processes, so that it is not surprising that others since by using methods different from Moissan's have not obtained diamonds. Ruff used special tests to distinguish the crystals from silicon carbide, etc., and proved that they were diamonds.

Diamonds are found mainly in India, South America and South Africa (where they occur in vertical "pipes" of *blue ground*, from which they are separated by weathering and washing).

Colourless diamonds are almost chemically pure carbon; they are cut for gems by means of a revolving metal disc covered with diamond powder and oil. The diamond is exceedingly hard and black diamonds (*carbonado* or *boart*) are used for rock-drills or when crushed for cutting and polishing clear diamonds. Diamond is very inert and resists the action of most chemical reagents. When strongly heated in air or oxygen, however, it burns. Macquer in 1771 noticed that a burning diamond is surrounded by a small *flame*, showing that gaseous carbon monoxide CO is formed and burns to carbon dioxide. Diamond is also attacked by sulphur at 1000° and by fused sodium carbonate:

$\text{Na}_2\text{CO}_3 + \text{C} = \text{Na}_2\text{O} + 2\text{CO}$, and is slowly oxidised by a hot solution of potassium dichromate in concentrated sulphuric acid.

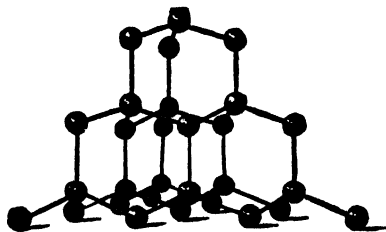


FIG. 162.—Linking of carbon atoms in diamond.

Diamond crystallises in the form of octahedra, the natural crystals having curved faces. By means of the X-rays, the arrangement of the atoms of carbon in diamond is found to be that shown in Fig. 162.

Each atom is joined to four others by four valencies of equal length, so that the four atoms surrounding the central atom form the corners of a regular tetrahedron. The whole crystal consists of single atoms of carbon

linked together by strong valency bonds in this way, which explains its great hardness. The distance between the centres of carbon atoms in diamond is 1.54 Å.*

Graphite.—Graphite (Greek, *grapho*, I write), also called *plumbago* or *black lead*, is a soft steel-grey or black mineral (found in Siberia, Ceylon and Bohemia) which marks paper and is used in making "lead pencils" (which contain no lead). It crystallises in the hexagonal system. Graphite is also deposited from solutions of carbon in molten iron (see above) and is therefore sometimes found in blast furnaces in the form of *kish*. Graphite is formed when charcoal is very strongly heated and diamond is also converted into graphite at a very high temperature. Graphite is obtained artificially by the Acheson process, in which a mixture of sand and powdered anthracite or coke is very strongly heated by an electric current passing through carbon rods embedded in the mass (Fig. 163). Graphite electrodes are produced by a similar process. This

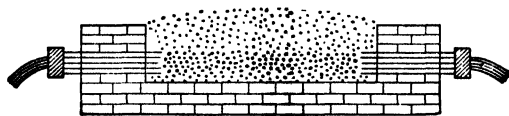


FIG. 163.—Electric graphite furnace.

artificial graphite is more expensive than natural graphite; it is very soft and pure and is used in suspensions in water (*Aquadag*) or oil (*Oildag*) as a lubricant.

Graphite unlike other non-metals is a good conductor of heat and electricity. It burns only at a high temperature and on account of its refractory character is used in polishing iron which is exposed to heat, and mixed with clay in making plumbago crucibles. Graphite is scarcely attacked by most reagents but a mixture of concentrated nitric and sulphuric acids and potassium chlorate slowly converts it in the cold into a curious substance called **graphitic acid**, discovered by Brodie in 1859; it contains carbon, oxygen and hydrogen. On heating, graphitic acid decomposes violently leaving a black powder of pure graphite. Diamond is not attacked by the oxidising reagent and charcoal yields little or no graphitic acid.

Examination by the X-rays shows that in graphite crystals the carbon atoms are arranged in hexagonal rings in parallel planes, each atom being linked to three others in the plane by valency bonds. The fourth valency bond links an atom in one plane to another in a parallel plane as shown in Fig. 164, and these linkages are weak, so that the planes readily slip under the application of force, which is said to explain the lubricating

* 1 Ångström unit = Å = 10^{-8} cm.

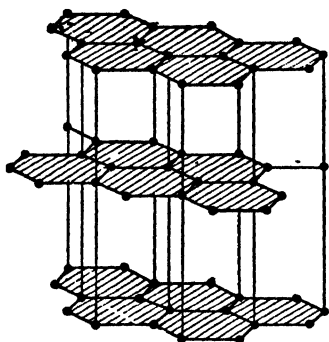


FIG. 164.—Linking of carbon atoms in graphite.

properties of graphite. The distance between the centres of carbon atoms in the rings is 1.4 Å, that between the planes is 3.4 Å. (It should be noticed that the rings in successive planes are not in register.)

The heats of combustion ($C + O_2 = CO_2$) (see p. 393) for 12.01 gm. of carbon at 0° C. and 1 atm. pressure are (Rossini and Jessup, 1938): graphite 94.030 k. cal. and diamond 94.484 k. cal. Graphite is the stable form at room temperature and the heat of transition of diamond to graphite is 0.454 k. cal. The heat of combustion of "amorphous" carbon is distinctly higher, 96.342 k. cal. at

1 atm. and 25° C. for hydrogen-free anthracite coke, and hence this is the least stable form.

Charcoal.—Besides the well-defined crystalline forms of diamond and graphite, there are several black varieties of carbon classed together as "amorphous carbon". Some at least are found by X-ray examination to contain microscopic crystals of graphite and the view has been expressed that they consist entirely of such crystals. Since X-ray examination will not indicate an amorphous form, it is not proved that this form is absent, and some authorities consider that the properties of "amorphous carbon" indicate the presence of an amorphous form.

It will be convenient to classify all these varieties under the name of "charcoal". Many of them contain impurities, especially hydrogen. The purest form of charcoal is obtained by heating pure ash-free cane sugar in a closed crucible, removing the hydrogen from the product by heating it strongly for several hours in a current of chlorine, washing with distilled water, drying and heating in a current of dry hydrogen till no more hydrogen chloride is evolved.

The following varieties of "amorphous" carbon are recognised:

- (1) *Charcoal*, from wood, sugar, etc.
- (2) *Lampblack*, *i.e.* soot from burning oils, fats, resin, natural gas (methane), acetylene, etc.
- (3) *Animal charcoal*, as bone charcoal, ivory black, etc.
- (4) *Coke*, obtained by carbonising coal; anthracite is a coal very rich in carbon, a kind of natural coke.
- (5) *Gas carbon*, deposited in retorts in making coal gas (p. 409).

- (6) *Electrode carbon*, artificially prepared by heating a mixture of anthracite, petroleum coke, etc., with pitch or other "bonder" at a temperature below that at which graphitising occurs.

These varieties are all black and opaque; their density and hardness depend largely on the temperatures at which they have been produced.

On oxidation with boiling alkaline potassium permanganate solution they form oxalic acid and mellitic acid $C_6(COOH)_6$, and since the latter (which occurs as the aluminium salt in the mineral *honey-stone*) is a derivative of benzene, it is probable that the carbon atoms in charcoal are linked in 6-membered rings as in graphite (see Fig. 164). Graphite is not oxidised by permanganate solution.

Wood charcoal, which is used as fuel in countries where wood is abundant, is prepared from wood by "carbonisation", *i.e.* decomposition by heat into volatile parts and non-volatile charcoal.

The process is carried out: (a) in pits or heaps (*meilers*) and (b) in closed ovens or retorts.

Charcoal-burning in *meilers* is very old and is described by Theophrastus (315 B.C.). A rough central chimney is built and billets of wood stacked round it in a conical pile, the whole being covered in with turf (Fig. 165). A lighted faggot is dropped down the chimney to kindle

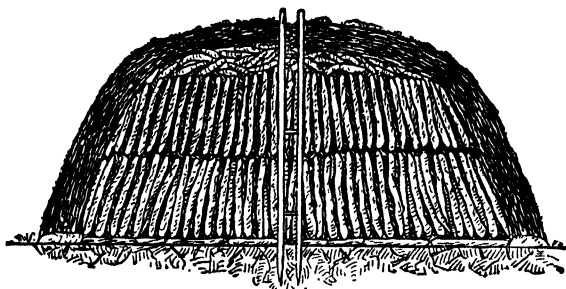


FIG. 165.—Charcoal meiler.

the wood, which burns *slowly*, just sufficient air being admitted through holes at the bottom. After some days the luminous flame from the chimney is replaced by a blue flame of carbon monoxide, when all the air-holes are stopped up and the charcoal is allowed to cool.

In the modern process (based on Glauber's work) the wood is heated in externally fired ovens or iron retorts from which air is excluded. The volatile liquid products are collected and the inflammable gas is used for heating the retorts. The liquid distillate consists of (a) a watery portion, the so-called *pyroligneous acid*, containing water, acetic acid, methyl alcohol, and acetone, which are extracted; (b) tar, which is valuable (*e.g.* Stockholm tar from pine wood).

Wood charcoal is a black amorphous friable material, retaining more or less the original shape of the wood but diminished in volume. Although the specific gravity of air-free charcoal is 1.3 to 1.9, the mass is very porous and floats on water. If the air is removed by placing the charcoal in water in a bottle connected with an air pump, the charcoal gives out bubbles and sinks. Charcoal is very permanent on exposure to air and moisture; charred oak stakes planted in the bed of the Thames by the Britons to resist the advance of Julius Caesar were found nearly two thousand years later and still sound at heart.

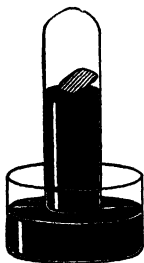


FIG. 166.—Adsorption of ammonia gas by charcoal.

In virtue of its great porosity charcoal readily takes up gases, the process being called **adsorption** since the gas is condensed on the surface of the charcoal, including the internal surface of the pores.

If a piece of recently ignited wood charcoal is passed into a tube of ammonia gas standing over mercury (Fig. 166), the gas rapidly disappears; the charcoal takes up about ninety times its volume of ammonia gas.

The volumes at S.T.P. of different gases adsorbed by 1 vol. of recently ignited coconut charcoal are :

Ammonia	-	-	-	171.7	Phosphine	-	-	-	69.1
Cyanogen	-	-	-	107.5	Carbon dioxide	-	-	-	67.7
Nitrous oxide	-	-	-	86.3	Carbon monoxide	-	-	-	21.2
Methyl chloride	-	-	-	76.4	Oxygen	-	-	-	17.9
Ethylene	-	-	-	74.7	Nitrogen	-	-	-	15.2
Nitric oxide	-	-	-	70.5	Hydrogen	-	-	-	4.4

The order in each half of the table is very nearly that of the boiling points, the more easily liquefiable gas being more adsorbed. The adsorptive power of charcoal is greatly increased by cooling in liquid air.

When a small crucible containing recently heated and nearly cold powdered wood charcoal is put into a jar of hydrogen sulphide it adsorbs much of this gas on standing for a few minutes. On taking out the crucible and inserting it into a jar of oxygen, the hydrogen sulphide is oxidised and the charcoal soon takes fire. Chlorine adsorbed on charcoal combines with hydrogen in the dark.

A very active form of charcoal is prepared by heating coconut shell; "active charcoal" used in respirators or "gas-masks" is obtained by heating wood charcoal prepared at 850° to 900° in a stream of air or steam, when the material obstructing the pores is removed. A good respirator carbon can also be made from coal. Active charcoal is also obtained by carbonising wood which has been treated with salts such as

zinc chloride or magnesium chloride, which are removed from the charcoal by washing with water or acids. It adsorbs much larger volumes of gas than ordinary charcoal. Active charcoal is also used for decolorising solutions and for removing fusel oil (amyl alcohol) from crude spirit.

Animal charcoal, also known as *bone black*, is prepared by the distillation of bones in iron retorts. The volatile products are gases, a watery liquid which contains ammonia, and *bone oil* or *Dippel's oil*. The residue in the retort is a black mass containing about 10 per cent. of carbon spread through a very porous body of calcium phosphate together with calcium carbonate, etc. If the phosphate and other salts are dissolved out by hydrochloric acid the charcoal remains as *ivory black*. Animal charcoal or blood charcoal is used in decolorising sugar syrup, although active wood charcoal is now used for this purpose. This action may be illustrated by boiling some indigo solution with powdered animal charcoal and filtering. The liquid runs through colourless.

The decolorising charcoal is revived by boiling it with caustic soda solution and washing. Bone black is revived by heating to redness in closed retorts.

Lampblack is a fine variety of soot prepared for use as a pigment by burning petroleum, turpentine, tar, etc., in a limited supply of air and collecting the soot by deposition. A finer variety called *carbon black* is prepared for use as a pigment (Indian ink, etc.) or as a filler in rubber tyres by allowing the flame of natural gas to impinge on a moving metallic surface. *Gas black* is made from natural gas in the same way as lampblack, and *acetylene black* from acetylene. Common lampblack is used in making printing ink and as a pigment. It contains some oily impurities which can be removed by heating in chlorine.

Two varieties of amorphous carbon, *coke* and *gas carbon* (see p. 409), are derived from coal, and since some varieties of coal (anthracite) contain more than 90 per cent. of carbon they will be considered here.

Coal.—Coal * is a carbonaceous mineral which is the final result of a series of decompositions which have occurred in the presence of a limited supply of air, undergone by vegetable matter of the remote past. High pressure due to the weight of superimposed strata was probably also necessary in these changes. Some of the carbon, hydrogen and oxygen were eliminated as carbon dioxide, water, and methane (CH_4), and the residue became increasingly rich in carbon.

The first stage in the conversion of vegetable matter into coal is represented by *peat*, which consists of accumulations of vegetable matter,

* Bone and Himus, *Coal, its Constitution and Uses*, 1936; Stopes and Wheeler, *The Constitution of Coal*, H.M.S.O., 1918; J. B. Robinson, *The Chemistry of Coal*, 1919.

chiefly mosses and bog-plants, which have undergone partial change and still preserve evidences of organic structure, although the deeper layers may be more compact and homogeneous. The next stage is represented by *lignite* or *brown coal*, which is more compact than peat and is lustrous, although impressions and remains of vegetable fragments, leaves, etc., are still distinct and numerous.

The next stage leads to *bituminous coal*, i.e. common coal. Distinct evidence of vegetable origin is still present and the original plants are sometimes found fossilised. Bituminous coals burn with a bright smoky flame and are further divided into *caking* and *non-caking coals*, according as they do or do not soften and fuse together on burning or coking. *Cannel coal* is a compact non-lustrous variety, dull grey or black in colour, breaking with a conchoidal fracture and yielding a large amount of gas and little coke. Splinters of cannel coal burn like candles when ignited, hence the name. *Jet* is a hard lustrous variety of cannel coal.

Coal does not seem to contain much free carbon since a large fraction (up to 40 per cent.) is soluble in pyridine and appreciable amounts of hydrogen, oxygen, and nitrogen are present in coal.

A late stage in coal formation is *anthracite*, which is rich in carbon (over 90 per cent.) ; it has a high ignition point, usually a brilliant lustre and a conchoidal fracture ; it does not burn with a flame and gives very little smoke. It burns slowly and gives an intense heat. Anthracite occurs locally in many coal-fields, such as South Wales, Scotland and Pennsylvania. Graphite may represent the ultimate stage of the decomposition, since it always contains a little hydrogen.

The following table shows the change in composition which occurs during the conversion of woody matter into coal, with the corresponding increase in calorific value (see below). The British thermal unit (B.Th.U.) is the amount of heat required to raise the temperature of 1 lb. of water through 1° F. Coals always contain about 1 or 2 per cent. of nitrogen.

	Carbon.	Hydrogen.	Oxygen.	Calorific Value B.Th.U. per lb.
Cellulose - - - -	44.5	6.2	49.3	7,500
Wood - - - -	50.0	6.0	44.0	7,400
Peat - - - -	60.0	5.9	34.1	9,900
Lignite - - - -	67.0	5.2	27.8	11,700
Bituminous coal - -	88.4	5.6	6.0	14,950
Welsh steam coal - -	92.5	4.7	2.8	15,720
Anthracite - - - -	94.1	3.4	2.5	15,720
Pure charcoal - - -	100.0			14,544
Petroleum - - - -	85.5	14.2	0.3	19,800
Coal gas - - - -				19,220
Hydrogen - - - -		100.0		62,100
Methylated spirit - -	52.2	13.0	34.8	11,160

(The values for wood, peat, etc., refer to materials free from moisture : the actual materials contain water and the calorific values are smaller than those given. The values for pure charcoal, coal gas, hydrogen, methyated spirit, and petroleum are given for comparison.)

Calorific value of a fuel.—The heat of combustion of a fuel such as coal is determined by burning a weighed amount of it inside a strong metal bomb (called a *bomb calorimeter*) (Fig. 167) containing compressed oxygen.

The coal is contained in a platinum crucible and is ignited by a small spiral of iron wire heated by an electric current. (The known heat of combustion of the iron is subtracted from the total heat evolved.) The bomb is immersed in water in a calorimeter and the rise in temperature of the water is measured by a delicate thermometer. The calculation, which involves the "water equivalent" of the apparatus, is made in the usual way. The result is usually called the calorific value of the fuel and is given as the number of heat units produced by the combustion of unit weight of fuel. The calculation may take account of the condensation of the water vapour produced in the combustion ("high value") or not ("low value"); in actual practice the water vapour will not usually be condensed and its latent heat will not be available. The calorific power of gas is determined by burning in a special calorimeter of ingenious construction so that the calorific value is continuously and automatically registered by the apparatus itself.

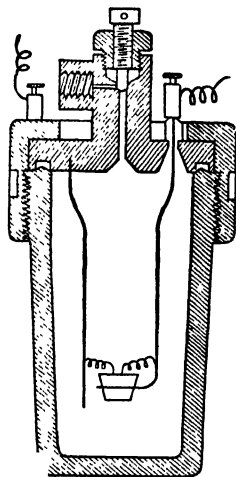


FIG. 167.—Bomb calorimeter.

THERMOCHEMISTRY *

The evolution of heat in many chemical reactions, in some cases appearing as active combustion, is of great importance. Most of the energy expended in daily life proceeds from the combustion of coal or mineral oil, in other words from chemical processes.

The heat Q_v evolved in a chemical reaction occurring *at constant volume* (so that no work is done against the pressure of the atmosphere) is a measure of the diminution of energy, *i.e.* the energy of the initial system E_1 minus the energy of the final system E_2 :

$$Q_v = E_1 - E_2 = -\Delta E. \dots\dots\dots (1)$$

The **heat of reaction** is defined as the quantity of heat evolved at constant volume or constant pressure when the quantities in grams of the initial

* See Partington and Stratton, *Intermediate Chemical Calculations*, Chapter IX.

substances react completely to form the final substances according to the chemical equation, and the final products are brought to the same temperature as the initial substances.

The heat is measured in gram calories (g. cal.) or kilogram calories (k. cal.). 1 g. cal. is the heat required to raise the temperature of 1 gm. of water by 1° C., and 1 k. cal. = 1000 g. cal..

In reactions involving gases changes of volume may occur, and hence work is done by the pressure of the atmosphere on the system if there is a contraction, or is spent by the system in overcoming that pressure if there is an expansion. If there is contraction the evolution of heat is greater by the thermal equivalent of the external work than it would have been if no change of volume had occurred. If there is expansion the heat evolved is diminished by that part of the energy of the system which would otherwise have appeared as heat, but now leaves the system as external work spent in overcoming pressure.

If the initial volume is V_1 and the final volume V_2 , the work spent by the system in overcoming the constant external pressure p is $p(V_2 - V_1)$. If Q_p is the heat of reaction at constant pressure, we have (when heat and work are measured in the same units):

$$Q_p + p(V_2 - V_1) = Q_v.$$

If $H = U + pV$ is the heat content, the diminution of heat content is:

$$Q_p = H_1 - H_2 = -\Delta H. \dots\dots\dots(2)$$

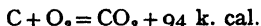
Equations (1) and (2) show that the heat of reaction at constant volume or at constant pressure, respectively, depends only on the initial state (defined by E_1 or H_1) and the final state (defined by E_2 or H_2) of the system. This is equivalent to the statement:

If a reaction at constant volume or constant pressure is carried out in stages, the algebraic sum of the amounts of heat evolved in the separate stages (heat absorbed being reckoned negative) is equal to the total evolution of heat when the reaction occurs directly.

This is a simple consequence of the Law of Conservation of Energy and is known as **Hess's Law of constant heat summation** (1840). It enables us to calculate many heats of reaction which could not be determined directly.

EXAMPLE.—Find the heat of formation per mol of carbon monoxide CO from solid carbon and gaseous oxygen given the following data:

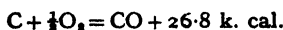
Heat of combustion of carbon to carbon dioxide:



Heat of combustion of carbon monoxide to dioxide:



By subtracting the second of these equations from the first, we find the heat of formation of carbon monoxide:



By means of Hess's Law all heats of reaction may be calculated from the heats of formation of the compounds concerned. The **heat of formation** of a compound is the quantity of heat evolved during the formation of 1 mol (molecular weight in grams) of the compound *from its elements*. The substances must be in specified states and the products must be brought to the same temperature as the initial substances. The heat of formation may refer to a reaction at constant volume or (as in the table below) at constant pressure.

Reactions in which heat is evolved are called **exothermic reactions**, those in which heat is absorbed **endothermic reactions**. If a compound is formed from its elements with evolution of heat it is called an **exothermic compound**; if formed from its elements with absorption of heat it is called an **endothermic compound**.

HEATS OF FORMATION

$(\text{H}_2) + \frac{1}{2}(\text{O}_2) = \text{H}_2\text{O}$	68.5	$2[\text{P}] + \frac{5}{2}(\text{O}_2) = [\text{P}_2\text{O}_5]$	360
$(\text{H}_2) + \frac{1}{2}(\text{O}_2) = (\text{H}_2\text{O})$	57.8	$[\text{C}] + (\text{O}_2) = (\text{CO}_2)$	94
$(\text{H}_2) + (\text{O}_2) = \text{H}_2\text{O}_2$	45.2	$[\text{C}] + \frac{1}{2}(\text{O}_2) = (\text{CO})$	26.8
$\frac{1}{2}(\text{H}_2) + \frac{1}{2}(\text{Cl}_2) = (\text{HCl})$	22.0	$[\text{C}] + 2[\text{S}] = \text{CS}_2$	-15
$\frac{1}{2}(\text{H}_2) + \frac{1}{2}\text{Br}_2 = (\text{HBr})$	8.6	$[\text{Na}] + \frac{1}{2}(\text{Cl}_2) = [\text{NaCl}]$	98.3
$\frac{1}{2}(\text{H}_2) + \frac{1}{4}[\text{I}_2] = (\text{HI})$	-6.0	$[\text{Na}] + \frac{1}{2}\text{Br}_2 = [\text{NaBr}]$	86.7
$(\text{H}_2) + [\text{S}] = (\text{H}_2\text{S})$	5.3	$[\text{Na}] + \frac{1}{2}[\text{I}_2] = [\text{NaI}]$	69.1
$\frac{1}{2}(\text{N}_2) + \frac{3}{2}(\text{H}_2) = (\text{NH}_3)$	11	$[\text{Ag}] + \frac{1}{2}(\text{Cl}_2) = [\text{AgCl}]$	30.6
$[\text{P}] + \frac{3}{2}(\text{H}_2) = (\text{PH}_3)$	-5.8	$[\text{Ag}] + \frac{1}{2}\text{Br}_2 = [\text{AgBr}]$	24
$[\text{As}] + \frac{3}{2}(\text{H}_2) = (\text{AsH}_3)$	-44	$[\text{Ag}] + \frac{1}{2}[\text{I}_2] = [\text{AgI}]$	15
$\frac{1}{2}(\text{N}_2) + \frac{1}{2}(\text{O}_2) = (\text{NO})$	-21.6	$[\text{Ca}] + (\text{Cl}_2) = [\text{CaCl}_2]$	191
$(\text{N}_2) + \frac{1}{2}(\text{O}_2) = (\text{N}_2\text{O})$	-19.71	$[\text{Sr}] + (\text{Cl}_2) = [\text{SrCl}_2]$	198
$[\text{S}] + (\text{O}_2) = (\text{SO}_2)$	71	$[\text{Ba}] + (\text{Cl}_2) = [\text{BaCl}_2]$	205
$[\text{S}] + \frac{3}{2}(\text{O}_2) = (\text{SO}_3)$	94	$[\text{Fe}] + \frac{3}{2}(\text{Cl}_2) = [\text{FeCl}_3]$	96

The values are in k. cal. for room temperature and 1 atm. Round brackets () denote that the substances are gases, square brackets [] that they are solids; liquids are written without brackets. Sulphur is the rhombic (α) form, carbon is taken as graphite.

If we suppose all the compounds on the left of an equation to be decomposed into their elements, an amount of heat is absorbed equal to the algebraic sum of the heats of formation of these compounds. If we now suppose the elements to be combined to form the compounds on the right of the equation, an amount of heat is evolved equal to the algebraic sum of the heats of formation of these compounds. It follows from Hess's law that:

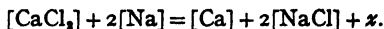
Heat of reaction = sum of heats of formation of final compounds - sum of heats of formation of initial compounds.

The energies of the compounds are all referred to those of the elements as zero. The amounts of energy associated with the different elements

are not of course zero, nor are they equal, but it is only the difference between the amounts of energy associated with the elements when in combination and when free that is required.

Thus, the thermochemical equation $[\text{Cu}] + (\text{Cl}_2) = [\text{CuCl}_2] + 51.6 \text{ k. cal.}$ may be written in the form : $0 + 0 = [\text{CuCl}_2] + 51.6 \text{ k. cal.}$, or $[\text{CuCl}_2] = -51.6 \text{ k. cal.}$, indicating that $[\text{CuCl}_2]$ contains 51.6 k. cal. less energy than $[\text{Cu}] + (\text{Cl}_2)$. *The symbols of compounds thus represent quantities of energy which may be added or subtracted.* We may write the *negative* values of the heats of formation instead of the chemical symbols and solve for the unknown heat of reaction.

EXAMPLE.—Find the heat of the reaction :



The heats of formation of CaCl_2 and NaCl are 191 k. cal. and 98.3 k. cal. respectively, hence :

$$-191 = -2 \times 98.3 + x, \text{ or } x = 5.6 \text{ k. cal.}$$

If substances are produced in aqueous solution we have to take account of **heats of solution**. These vary with the amount of water but become constant when this is very large ; we usually suppose so much water taken that the heat of solution is constant. This amount of water is denoted by Aq. Thus : $(\text{NH}_3) + \text{Aq.} = \text{NH}_3 \text{ Aq.} + 8400 \text{ g. cal.}$ means that when 17 grams of ammonia gas dissolve in a large quantity of water 8400 g. cal. are evolved. If still more water is added no heat change occurs, hence Aq. does not need to be specially stated.

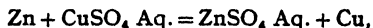
EXAMPLE.—Find the heat of formation of gaseous hydrogen iodide from hydrogen and solid iodine from the following heats of reaction :

1. $(\text{HI}) + \text{Aq.} = \text{HI Aq.} + 19.20 \text{ k. cal.}$
2. $\text{KOH Aq.} + \text{HI Aq.} = \text{KI Aq.} + 13.57 \text{ k. cal.}$
3. $\text{KI Aq.} + \frac{1}{2}(\text{Cl}_2) = [\text{I}] + \text{KCl Aq.} + 26.21 \text{ k. cal.}$
4. $\text{KOH Aq.} + \text{HCl Aq.} = \text{KCl Aq.} + 13.74 \text{ k. cal.}$
5. $\frac{1}{2}(\text{H}_2) + \frac{1}{2}(\text{Cl}_2) = (\text{HCl}) + 22.0 \text{ k. cal.}$
6. $(\text{HCl}) + \text{Aq.} = \text{HCl Aq.} + 17.32 \text{ k. cal.}$

We write (4), (5) and (6) in the reverse order underneath (1), (2) and (3) and add all the equations, when we find :

$$\frac{1}{2}(\text{H}_2) + [\text{I}] = (\text{HI}) - 5.93 \text{ k. cal.}$$

Free energy.—Although the heat evolution or diminution of **total energy** gives an approximate measure of the stability of a compound, it is really the content of **free energy** which determines this. Of the total energy diminution part is in general convertible into work by suitable means, whilst the other part appears as heat. The part convertible into work is the free energy. For example, the reaction :



as it occurs in the ordinary way evolves heat, but when it occurs in the

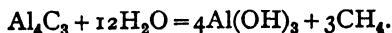
Daniell cell part of the energy change is obtainable as electrical energy, which in turn is (theoretically) completely convertible into work. It is this free energy change which provides an accurate measure of the tendency of the system $\text{Zn} + \text{CuSO}_4 \text{ Aq.}$ to pass spontaneously into the system $\text{Cu} + \text{ZnSO}_4 \text{ Aq.}$, i.e. which provides a measure of the relative stability of the two systems. *Only those changes can occur spontaneously which are attended by a diminution of free energy.* The corresponding statement for the total energy, to the effect that only those reactions occur spontaneously which are attended by evolution of heat, was stated by Thomsen and Berthelot, although the latter had the correct idea in mind when he called it the **principle of maximum work**. This principle is very often approximately true and is a useful guide. It is true at the absolute zero and in many reactions between solids and liquids it holds approximately. The correct statement of the principle forms what is known as **Nernst's Heat Theorem** (1906); this enables us in many cases to calculate equilibrium constants from heats of reaction.

COMPOUNDS OF CARBON AND HYDROGEN

Compounds of carbon and hydrogen are called **hydrocarbons** and very many are known. Their study belongs to Organic Chemistry, where they are classified in series; the simplest members of three series are: methane CH_4 , the parent of the *paraffin series* $\text{C}_n\text{H}_{2n+2}$; ethylene C_2H_4 , the parent of the *olefines* C_nH_{2n} ; and acetylene C_2H_2 , the simplest member of the acetylene series $\text{C}_n\text{H}_{2n-2}$.

Methane.—Methane CH_4 , discovered by Volta in 1776, occurs mixed with carbon dioxide in *marsh gas*, which is formed by the bacterial decay of vegetable matter at the bottom of stagnant pools and is liberated in bubbles when the mud is stirred. Methane is also contained in coal and when the pressure is removed it escapes in the mines as *fire-damp*. This explodes when its mixture with air is kindled. The gas issuing from "blowers" or fissures in coal may contain 80 to 98 per cent. of methane. *Natural gas* from petroleum wells contains over 90 per cent. of methane and is utilised for heating purposes. Coal gas contains about 25 to 35 per cent. by volume of methane, unless it has been mixed with water gas when the methane content is reduced by dilution.

Methane is formed in very small amounts by direct synthesis when carbon is heated in hydrogen: $\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$. It is formed by the action of water on aluminium carbide:



The gas is passed through potassium permanganate solution to remove acetylene but still contains a little free hydrogen; it may be freed from this by mixing with oxygen and passing first over palladium black and then through alkaline pyrogallol.

Methane is usually prepared in the laboratory by heating in a hard glass (or better, copper) flask anhydrous sodium acetate with three times its weight of soda-lime :

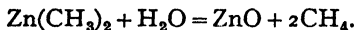


The methane is collected over water, in which it is almost insoluble.

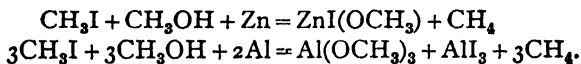
The anhydrous sodium acetate is made by heating the crystalline salt on a clean sand-bath until the water is driven off and the salt fuses, when it is cooled and powdered. The soda-lime is made by slaking quicklime with concentrated sodium hydroxide solution and drying ; it is less fusible than sodium hydroxide and does not attack glass so easily.

The gas so prepared is not very pure and may contain up to 8 per cent. of hydrogen and some ethylene.

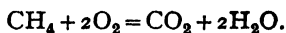
Pure methane may be prepared by the action of water on liquid zinc methyl :



Since zinc methyl is spontaneously inflammable this method is not very convenient, and pure methane is best prepared by dropping a solution of methyl iodide in methyl alcohol on zinc-copper couple,* or on amalgamated aluminium foil, the gas being passed through a tube of zinc-copper couple to free it from the vapour of methyl iodide :



Methane is a colourless odourless gas lighter than air, liquefied only with difficulty. It is combustible, burning in air with a feebly luminous flame to carbon dioxide and steam :



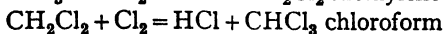
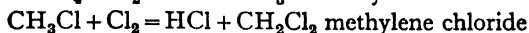
It forms an explosive mixture with air (even with only 6 per cent. of methane) or oxygen, the kindling of which causes explosions in mines. The poisonous *after-damp* formed contains carbon monoxide from the incomplete combustion of the methane in presence of an insufficient supply of oxygen :



A mixture of methane and chlorine burns when kindled with a green-edged smoky flame : $\text{CH}_4 + 2\text{Cl}_2 = \text{C} + 4\text{HCl}$. When a mixture of methane and chlorine is exposed to light the chlorine reacts by removing part or all of the hydrogen of the methane to form hydrogen chloride, and each atom of hydrogen removed is replaced by an atom of chlorine. Methane is a **saturated hydrocarbon**, *i.e.* all the valencies of the carbon

* The couple is made by pouring copper sulphate solution over granulated zinc and when sufficient copper is deposited, pouring off the solution and washing the couple with distilled water. It should be freshly made for use.

are linked with hydrogen atoms, and reaction cannot occur by addition but only by substitution. Four products are formed (p. 104) :



Methane is not easily attacked by reagents, hence the name "**paraffin**" (from the Latin *parum affinis*) for the group to which it belongs.

Ethylene.—Ethylene C_2H_4 , discovered by the Dutch chemists Deimann, Bondt, Lauwerenburgh and Paets van Troostwijk in 1795, is present in

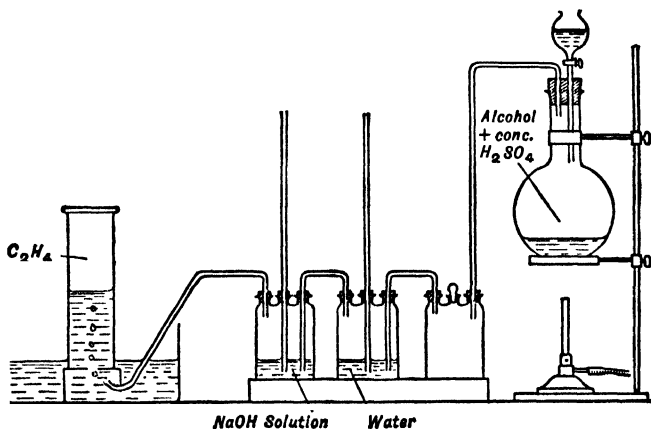
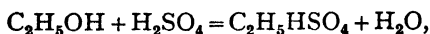
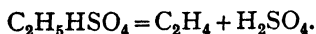


FIG. 168.—Preparation of ethylene.

raw coal gas. A small quantity of ethylene is formed by heating carbon in hydrogen. Ethylene is prepared in the laboratory by heating a mixture of alcohol and concentrated sulphuric acid. The reaction involves the removal of the elements of water from the alcohol $\text{C}_2\text{H}_5\text{O}$, and occurs in two stages. Ethyl sulphuric acid is first formed :

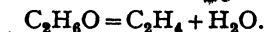


and on heating in the presence of concentrated sulphuric acid this decomposes :



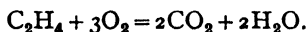
A mixture of 30 c.c. of alcohol and 80 c.c. of concentrated sulphuric acid is carefully heated in a 1 litre flask (since the mixture froths) and when the evolution of gas slackens a mixture of equal volumes of alcohol and concentrated sulphuric acid is run into the flask from a tap-funnel. The gas is passed through an empty Woulfe's bottle and then through water and sodium hydroxide solution in Woulfe's bottles to remove carbon dioxide and sulphur dioxide, and is collected over water (Fig. 168).

Ethylene may also be prepared by passing alcohol vapour over heated thorium oxide, alumina or kaolin, which act as catalysts ; or by passing alcohol vapour through syrupy orthophosphoric acid previously evaporated until it boils at 220° . In these preparations the gas is passed through a U-tube cooled in a freezing mixture to remove alcohol vapour :

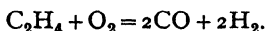


Ethylene is now made in large quantities by "cracking" petroleum or natural gas, *i.e.* decomposing by heat in the vapour phase, the ethylene being extracted by dissolving in acetone. It is made into a great variety of synthetic organic chemicals.

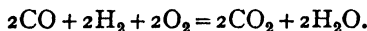
Ethylene is a colourless gas with a peculiar sweet smell ; it is not poisonous and has anaesthetic properties. It is more soluble than methane in water. It burns in air with a luminous smoky flame, forming carbon dioxide, steam and a little free carbon. Its mixture with air or oxygen explodes *violently* when kindled :



When mixed with its own volume of oxygen and exploded by a spark, only the carbon burns to carbon monoxide and the hydrogen is set free :

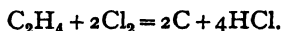


The gaseous product when mixed with half its bulk of oxygen can again be exploded by a spark :

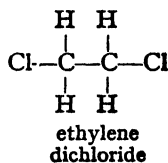
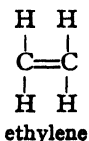
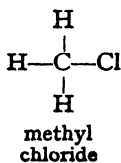
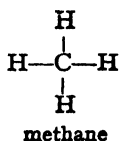


With methane, the least proportion of oxygen which can form an explosive mixture is an equal volume (p. 398).

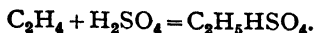
A mixture of ethylene and chlorine when kindled burns with a very smoky red flame, clouds of carbon and fumes of hydrogen chloride being emitted from the jar :



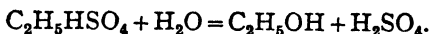
Ethylene differs from methane in being an **unsaturated hydrocarbon** ; the two atoms of carbon in its molecule are linked by a double bond and for this reason the molecule will form compounds by direct addition instead of by substitution, as in the case of a saturated hydrocarbon. This is clear from the structural formulae :



When a mixture of equal volumes of ethylene and chlorine is exposed to light, combination occurs and an oily liquid ethylene dichloride is formed: $\text{C}_2\text{H}_4 + \text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl}_2$. For this reason ethylene was called *olefiant* (oil-forming) *gas* by Fourcroy. Ethylene is absorbed by concentrated sulphuric acid on shaking and ethyl sulphuric acid is formed:



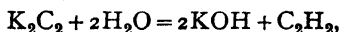
When this is boiled with water alcohol is formed:



Ethylene is more readily absorbed by fuming sulphuric acid or by bromine water; in the first case the compounds $\text{C}_2\text{H}_4\text{H}_2\text{S}_2\text{O}_7$ and $\text{C}_2\text{H}_4\cdot 2\text{SO}_3$ are formed; in the second case ethylene dibromide $\text{C}_2\text{H}_4\text{Br}_2$ is produced.

Ethylene does not combine with hydrochloric acid, but it combines with hydrobromic and hydriodic acids to form ethyl bromide $\text{C}_2\text{H}_5\text{Br}$, and ethyl iodide $\text{C}_2\text{H}_5\text{I}$, respectively. It combines with hydrogen in presence of platinum black to form ethane C_2H_6 , a saturated hydrocarbon of the paraffin series.

Acetylene.—A familiar compound of carbon and hydrogen is the gas acetylene C_2H_2 , prepared for use in blowpipes (p. 113) by the action of water on calcium carbide. It was discovered by Edmund Davy in 1836, by the action of water on potassium carbide:

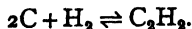


but was first carefully studied by Berthelot, who showed that it is formed when ethylene or alcohol vapour is passed through a red-hot tube.



FIG. 169.—Berthelot's synthesis of acetylene.

Berthelot in 1862 also discovered the *direct synthesis* of acetylene from its elements when an electric arc burns between carbon poles in an atmosphere of hydrogen (Fig. 169):



Acetylene is produced when a bunsen burner, whether of the laboratory type or in gas-stoves or gas-rings, "strikes back", *i.e.* when the coal gas burns at the small jet in a limited supply of air and in contact with the metal tube, which cools the flame. The peculiar smell noticed is usually said to be due to the presence of acetylene.

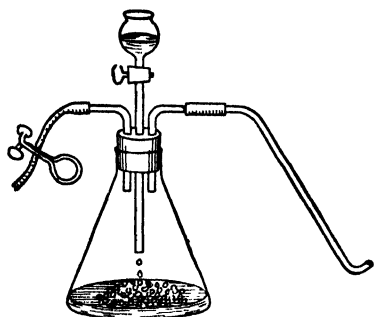
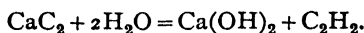


FIG. 170.—Preparation of acetylene.

The formation of acetylene in the gas issuing from the burner is detected by holding over it a large globe which is then wetted inside with an ammoniacal solution of cuprous chloride. The dark blue liquid rapidly becomes covered with a red film, owing to the precipitation of cuprous acetylide Cu_2C_2 , an explosive substance. This is formed in larger quantity by passing acetylene into the solution.

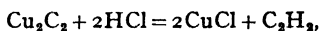
Acetylene is best prepared by dropping water on calcium carbide supported on a layer of sand, the air being first displaced from the flask by coal gas (Fig. 170). This reaction was discovered by Wöhler in 1862 :



Various types of special generators for the gas are used when it is required for lighting purposes.

The acetylene prepared from commercial calcium carbide may contain hydrogen sulphide and phosphine, from which it may be purified by passing through sodium hydroxide solution and acidified copper nitrate solution.

Pure acetylene may be prepared by the action of concentrated hydrochloric acid on cuprous acetylide :



or by heating ethylene dibromide with alcoholic potash (or, better, with sodium ethoxide) and passing the gas through a second flask containing boiling alcoholic potash :

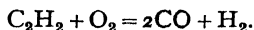


Acetylene is a colourless gas which is said to have an ethereal odour when pure but usually has an unpleasant smell. The pure gas is said to be non-poisonous and to have anaesthetic properties. It is soluble in its own volume of water, is more soluble in alcohol, and acetone dissolves 12 times its volume of acetylene at 15° and 100 times its volume under 12 atm. pressure. Acetylene is an endothermic substance and explodes when exposed to the shock of detonating mercury fulminate, breaking up into carbon and hydrogen. It may also explode when compressed, so that when stored under pressure the gas is absorbed

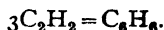
in liquid acetone soaked up in a porous material such as *kapok*, the seed hairs of a tree. Acetylene is chiefly used as an illuminant and in the oxyacetylene blowpipe for welding and cutting steel: it has been replaced to some extent for the latter by an oil gas (*blau gas*) rich in ethylene, or by coal gas.

Acetylene burns in air with a luminous very smoky flame, but when supplied to special burners it gives a very luminous white flame without smoke. A mixture of acetylene with oxygen, or even with air, when kindled *explodes with extreme violence* which may shatter even very strong glass vessels, so that it is unsafe to try the experiment with ordinary precautions. *The explosion of acetylene (or even ethylene) with oxygen should never be attempted in an ordinary eudiometer.*

In the oxyacetylene blowpipe, owing to the very high temperature, steam and carbon dioxide are dissociated so that the reaction is

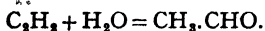


When heated to dull redness, acetylene undergoes polymerisation and some benzene is formed:



In this reaction a straight-chain (*aliphatic*) hydrocarbon is converted into a ring (*aromatic*) hydrocarbon, and since acetylene is easily obtained by direct synthesis from the elements this reaction amounts to a synthesis of benzene and thence of its numerous derivatives.

Acetylene in presence of mercuric bromide or sulphate as a catalyst takes up the elements of water, forming *acetaldehyde*:



From the latter, *alcohol* $\text{CH}_3\text{CH}_2\text{OH}$ is formed by reduction and *acetic acid* CH_3COOH by oxidation. These reactions have been used on the technical scale. By the regulated action of chlorine on acetylene in presence of other substances (*e.g.* sulphur chloride) various compounds of carbon, hydrogen, and chlorine may be formed which are really chlorinated hydrocarbons. They are largely used as solvents for oils, fats, resins, etc., under such names as *Westron* ($\text{C}_2\text{H}_2\text{Cl}_4$) and *Westrosol* (C_2HCl_3). *Westron* is also used as a solvent for cellulose acetate.

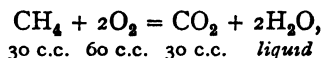
The composition of hydrocarbon gases.—The composition of methane, ethylene and acetylene is determined by explosion with excess of oxygen in a eudiometer. In the case of acetylene the explosion is very violent and special precautions must be taken; an ordinary eudiometer is certain to burst and there is danger of this also with ethylene. The volumes given below are, for simplicity of calculation, larger than should be used in actual experiments. Carbon dioxide and water are formed in the explosion of any hydrocarbon with excess of oxygen. The water

condenses on cooling and the carbon dioxide is absorbed from the residual oxygen by means of a solution of potassium hydroxide.

I. Let us suppose that 30 c.c. of *methane* are mixed with 66 c.c. of oxygen and exploded. After cooling to the original temperature and adjusting the pressure the residual volume is 36 c.c. This gas contains carbon dioxide and the residual oxygen. On treatment with potassium hydroxide a residue of 6 c.c. of oxygen is left. The volume of carbon dioxide formed is therefore 30 c.c. or 1 vol. of methane gives 1 vol. of carbon dioxide, *i.e.* 1 molecule of methane gives 1 molecule of carbon dioxide. The molecule of carbon dioxide contains 1 atom of carbon hence the molecule of methane contains 1 atom of carbon.

The volume of oxygen used is $66 - 6 = 60$ c.c. Of this, 30 c.c. have been used to burn the carbon, hence 30 c.c. of oxygen were used to burn the hydrogen. Therefore the hydrogen present in 30 c.c. of methane if free would be 60 c.c. Thus one molecule of methane contains two molecules or four atoms of hydrogen. The formula is therefore CH_4 . This may be *confirmed* by a measurement of the density of methane.

The contraction on explosion, $96 - 36 = 60$ c.c., is in agreement with the equation:



II. Suppose 30 c.c. of *ethylene* are mixed with 95 c.c. of oxygen and exploded. The volume after explosion is 65 c.c. After absorption with potassium hydroxide 5 c.c. of oxygen remain. Thus 60 c.c. of carbon dioxide were formed or 1 molecule of ethylene gives *two* molecules of carbon dioxide, *i.e.* the ethylene molecule contains two atoms of carbon. The oxygen required for the combustion of the carbon will be equal in volume to the carbon dioxide, *i.e.* 60 c.c. The total oxygen consumed is $95 - 5 = 90$ c.c., hence 30 c.c. were used for the combustion of the hydrogen. Hence the 30 c.c. of ethylene contained hydrogen equivalent to 60 c.c. of free hydrogen, or 1 molecule of ethylene contains 2 molecules of hydrogen, 2H_2 or H_4 . Hence the formula of ethylene is C_2H_4 . This may be *confirmed* by a measurement of the density of ethylene.

III. If 10 c.c. of *acetylene* are mixed with 30 c.c. of oxygen and exploded the residual gas occupies 25 c.c. After absorption with potassium hydroxide the contraction is 20 c.c. and 5 c.c. of oxygen remain. Thus 2 molecules of carbon dioxide have been formed from 1 molecule of acetylene or the latter contains *two* atoms of carbon. The oxygen consumed is $30 - 5 = 25$ c.c., hence the hydrogen has required $25 - 20 = 5$ c.c. of oxygen, corresponding with 10 c.c. of hydrogen. Thus the acetylene molecule contains its own volume of hydrogen, *i.e.* H_2 . Hence the formula of acetylene is C_2H_2 . This may be *confirmed* by a measurement of the density of acetylene.

If a mixture of methane, ethylene and acetylene is given, the acetylene may be absorbed by ammoniacal cuprous chloride (which would also absorb any carbon monoxide if present), and then the ethylene by fuming

sulphuric acid or bromine water. The composition of the residual methane may be checked by explosion with oxygen.*

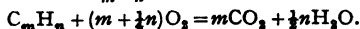
Coal gas.—The “carbonisation” or thermal distillation of coal with the formation of gas and coke was first carried out by the Rev. John Clayton in 1688, the results being published in 1739. The use of coal gas as an illuminant was introduced by William Murdoch in 1792; in 1798 he installed a gas plant for lighting the factory of Boulton and Watt at Soho near Birmingham. Gas lighting was introduced into Manchester factories in 1805, the first public gas-works being erected at Salford, and about the same time gas lighting was used on a very small scale in London. The Gas Light and Coke Co. was one of the first to supply coal gas. The streets of London were partly lighted by gas in 1808—an event which caused much ridicule and apprehension, and Paris followed in 1815. Houses were not lighted by gas until much later.

In the gas-works (Fig. 171) bituminous coal is “carbonised” in a row of horizontal fire-clay *retorts* heated by producer gas formed by passing air and steam over red-hot coke. The gas evolved from the coal passes from the retorts by way of vertical *ascension pipes* into one long horizontal *hydraulic main*, which serves as a water seal and prevents gas passing back when a retort is opened for charging with coal or removal of coke. In the hydraulic main partial separation occurs into crude gas, ammoniacal liquor and tar. The crude gas leaving the hydraulic main at about 60° contains the following impurities (which should be removed) in per cents. by volume :

Ammonia - - -	0.7 - 1.4	Hydrocyanic acid -	0.05 - 0.15
Hydrogen sulphide -	0.9 - 1.7	Carbon disulphide -	0.02 - 0.04

More tar is separated in the *condensers*, a series of air- or water-cooled iron pipes in which ammoniacal liquor is also separated with the tar, the liquids passing into the *tar-well*. After cooling the gas is passed to the *exhausters*, which maintain a slight vacuum to the retorts and force the gas forward through the subsequent purifying plant into the gas-holder. From the exhausters the gas passes to a *tar-separator* in which tar-fog is taken out, say by dividing the gas into fine streams which impinge on a solid surface to which the tar droplets adhere. The gas then passes to a *washer*, which may be an iron tower packed with boards set on edge over which water is run in the opposite direction to the gas flow. In the washer the rest of the ammonia is taken out and along with it

* An alternative to the above arithmetical argument is to assume that the formula of the hydrocarbon is C_mH_n and the combustion reaction is



(See Partington, *Text-Book*, Chap. XXXII). Reasoning in which separate symbols are used for *all* the gas volumes usually comes to grief in examination answers.

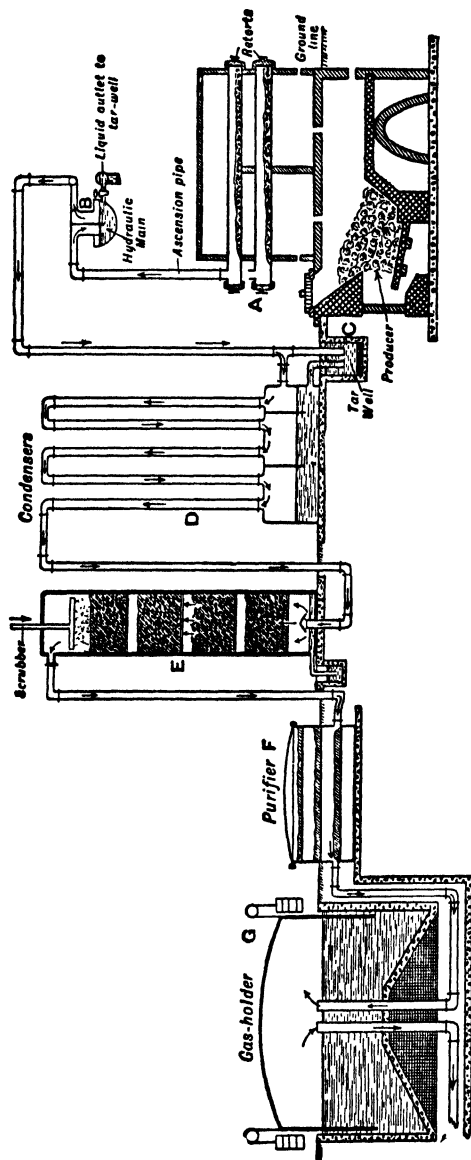
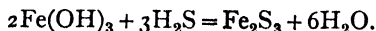


FIG. 171.—Diagram of a coal gas-works.

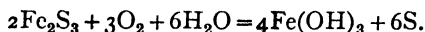
On the right two banks of horizontal fire-clay retorts 4 are shown in section. They are fitted with doors at each end to facilitate removal of coke, and are heated to about 1000° by gas made in the gas-producer shown below. The crude gas from the retorts passes to the hydraulic main, shown in cross-section at B, in which it is cooled to about 60° , and the liquid which separates passes to the tar-well C. The gas then passes through the air- or water-cooled pipes of the condensers D, in which it is cooled to atmospheric temperature and as a result more tar and ammoniacal liquor are separated and pass into the tar-well. After passing through exhausters and a tar-separator (not shown in the figure) the gas passes through washers or scrubbers E, the type shown being an iron tower containing coke packed in sections, over which a stream of water is passed downwards, the gas passing upwards. The washed gas then passes through the purifiers F, containing hydrated ferric oxide, in which the hydrogen sulphide is removed. The purified gas then passes into the gas-holder G, the one shown being of the wet type and drawn on a much smaller scale than the rest of the apparatus.

some hydrogen sulphide and carbon dioxide. Large rotary washers containing revolving brushes dipping into water are also used.

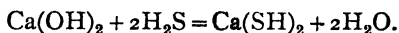
The scrubbed gas still contains as impurities upwards of 400 grains of sulphur in the form of hydrogen sulphide and 40 grains as carbon disulphide per 100 cu. ft. of gas. It passes to the *purifiers*, which are iron boxes containing hydrated ferric oxide ("bog iron ore") spread on shelves. The oxide decomposes the hydrogen sulphide with formation of ferric sulphide :



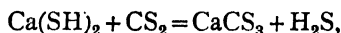
The "spent oxide" is "revivified" by exposure to air, when sulphur is separated and hydrated ferric oxide regenerated :



In small works the gas is passed over slaked lime which absorbs the hydrogen sulphide to form calcium hydrosulphide :



The carbon disulphide may then be taken out by passing the gas over "foul lime", previously used to remove hydrogen sulphide, when calcium thiocarbonate is formed :



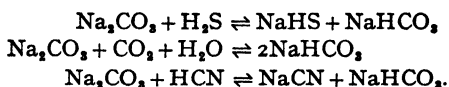
the hydrogen sulphide being taken out by a second purifier of lime (or iron oxide). If oxide purifiers are used the carbon disulphide may be removed by passing the gas over a heated nickel catalyst : $\text{CS}_2 + 2\text{H}_2 = \text{C} + 2\text{H}_2\text{S}$, the hydrogen sulphide being then taken out by an oxide purifier. Usually the carbon disulphide is taken out of the gas (see p. 409), since the sulphur dioxide formed on its combustion would lead to corrosion of metal fittings, etc.

The purified gas passes to the *gas-holder* ; the "wet" holder is a counterpoised iron bell sealed below by water ; the "dry" holder is an iron tower with a piston sealed round the edges by flowing tar so as to make it gas-tight. In many works the gas is dehydrated after purification by passing through concentrated calcium chloride solution, and the water in the holder is then covered by a film of a suitable oil to prevent rewetting of the gas.

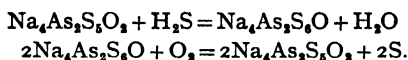
Carbonisation in large narrow vertical retorts of silica brick is now much used, more or less steam being introduced below to the retort, and the coke is cooled by the steam and is extracted continuously, the coal being also fed continuously to the top of the retort. In this way the coal gas is mixed with water gas formed by the action of steam on the red-hot coke, and even when horizontal retorts are used the gas is frequently mixed with water gas made separately.

The purified gas must contain less than 1 part of hydrogen sulphide per 10 millions, *i.e.* it should not blacken lead acetate paper in less than 3 minutes; in view of the carbon disulphide usually left in the gas, this seems an unnecessary refinement.

New liquid purification systems are coming into use instead of iron oxide. In one the hydrogen sulphide (with carbon dioxide and hydrocyanic acid) is absorbed in sodium carbonate solution, the hot solution being then exposed in a tower to a current of air, which reverses the absorption reactions:

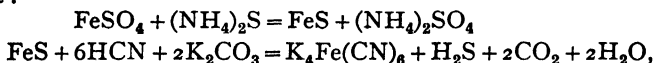


In the *Thylox process* a warm solution of sodium thioarsenate is used:

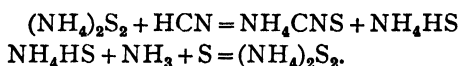


Other processes involve absorption of the hydrogen sulphide in triethanolamine $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ or in sodium phenoxide solution $(\text{C}_6\text{H}_5\text{ONa})$; in both cases the hydrogen sulphide is driven out again by steam.

The hydrocyanic acid HCN is recovered from the crude gas either as ferrocyanide by passing through a washer containing an alkali and an iron salt:



or as ammonium thiocyanate by passing through a washer containing ammoniacal liquor to which powdered sulphur is periodically added:



The spent oxide also contains Prussian blue; on heating with milk of lime this is converted into calcium ferrocyanide from which potassium ferrocyanide can be obtained by heating with potassium carbonate solution.

The average composition of genuine coal gas (unmixed with water gas) in volume percentages is:

Hydrogen	-	-	-	-	43	- 55	} "Diluents", non-illuminating but heat-producing.
Methane	-	-	-	-	25	- 35	
Carbon monoxide	-	-	-	-	4	- 11	
Olefines, acetylene and benzene	-	-	-	-	4.5	- 5	} Illuminants", unsaturated hydrocarbons.
Nitrogen (mostly from air leaks)	-	-	-	-	2	- 12	
Carbon dioxide	-	-	-	-	0	- 3	} "Inerts".
Oxygen	-	-	-	-	0	- 1.5	

The hydrogen in coal gas is formed by the thermal decomposition of gaseous hydrocarbons in contact with the hot walls of the retort. The carbon formed is deposited as **gas carbon**, a very pure form of amorphous carbon, which is a good conductor of electricity and is used for the pencils of arc lamps or in electric batteries.

In America *natural gas*, consisting chiefly of methane, is supplied from oil wells in pipes to consumers.

Crude benzene ("benzol") is usually extracted from coal gas or coke-oven gas by washing with a suitable oil, or adsorption in charcoal or silica gel, and is recovered. This reduces the carbon disulphide and sulphur compounds in the gas to half and also takes out about 95 per cent. of the naphthalene vapour present in the gas, which is an advantage as naphthalene in gas tends to deposit as a solid in the pipes and cause stoppages.*

The luminosity of genuine coal gas flames is due entirely to the 5 per cent. of olefine hydrocarbons, acetylene (0.06 to 0.07 per cent.), and benzene vapour. Modern coal gas burns with a flame of very mediocre luminosity as it is generally used only for heating purposes or with incandescent mantles for lighting.

The effect of such hydrocarbons on the luminosity of flames may be illustrated by fitting a small brass jet to each arm of a Y-tube, in one arm of which is a piece of cotton wool soaked in toluene (Fig. 172), attaching the tube to a hydrogen apparatus, and lighting the two jets. The hydrogen saturated with toluene vapour burns with a luminous flame.

Besides gas coke left in the retorts in gas-works and used as fuel, a very hard and compact form of coke is specially made for metallurgical purposes (blast furnaces) by carbonising coal in **coke ovens**. In the old "beehive ovens" part of the coal was burnt and the heat produced carbonised the rest, as in charcoal burning. In this way all the valuable by-products (tar, gas, ammonia and benzene) were lost. In the modern "recovery ovens" (Fig. 173) the coal is heated by gas in narrow fire-clay retorts, the gases evolved being collected and treated and the residual coke pushed out by rams and quenched by

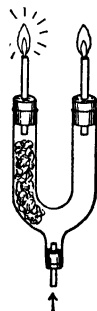
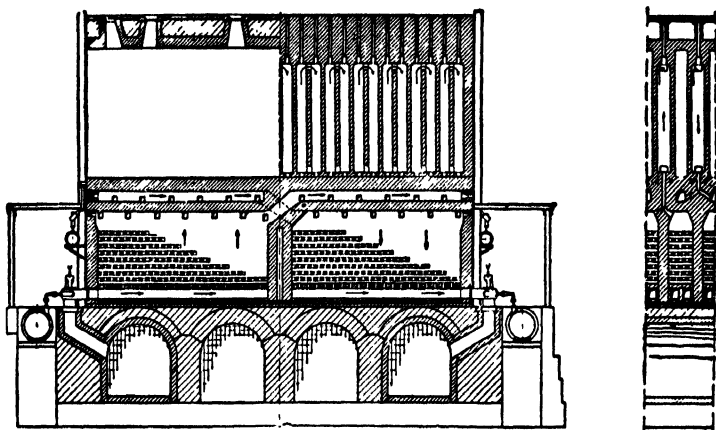


FIG. 172.—Luminosity imparted to hydrogen flame by toluene vapour.

* On gas manufacture see Hornby, *Text-book of Gas Manufacture*, 8th edit., 1920; J. Roberts, *Coal Carbonization*, 1927; W. B. Davidson, *Gas Manufacture*, 1923.



Courtesy of Coke Oven Managers' Association and Dr. R. A. Mott.

FIG. 173. Koppers coke-oven with "hair-pin" circulation flues and cross-over regenerator.

water. Such *oven coke* is hard enough to stand the weight of the blast furnace charge without crushing down.

FLAME *

In combustion reactions proceeding with the evolution of heat and light it is usual to distinguish between those attended by ignition only and those attended by the production of flame. An incandescent mass of fuel such as coke may burn without flame, but in addition to this there may be flames of carbon monoxide burning on the top of the mass. This example is typical of all others: a flame is produced only during the combustion of a gas or vapour and it may be formally defined as *a zone in which chemical reaction between gases is occurring, attended by the evolution of heat and light*. Flame is produced only in reactions which liberate considerable amounts of energy, sufficient to raise the gas to a very high temperature. This is not in itself sufficient to cause the emission of *light*, which seems to be a result of *chemical* reactions in the flame.

We distinguish between *luminous* and *non-luminous* flames. A flame of pure hydrogen burning in dust-free air emits hardly any visible light (Fig. 174); carbon monoxide burns with a bright blue flame. The alcohol flame of a spirit lamp and the bunsen flame are non-luminous whilst ethylene, acetylene, coal gas and candle flames are luminous.

The gas inside the flame is usually called the **combustible** and the gas outside the **supporter of combustion**. Liquids such as paraffin, and solids such as wax, can burn with flame only when they are first converted into gases or vapours, and this is the purpose of the *wick* in the lamp or candle. The oil or melted wax is raised by capillary attraction through the wick and enters the very hot space inside the flame. Here it is decomposed, forming combustible gases or vapours which then burn to produce the flame.

Unless the combustible gas and the supporter of combustion are first mixed together, the reaction between them will be limited to a region where they come in contact. Thus *flames are hollow*. This may be shown by the following experiments.

A piece of asbestos paper is lowered on a bunsen flame, when a scorched ring is formed. A match head thrust quickly inside a bunsen flame does not ignite for a considerable time. One end of a glass tube is inserted inside a bunsen flame: unburnt gas passes out of the tube and may be kindled at the upper end. The hollow character of flame was demonstrated by Hooke in 1676 by depressing a thin piece of mica on a candle flame, when the dark centre of unburnt gas is seen.

The functions of the combustible and supporter of combustion are purely relative, and depend simply on which gas is inside and which outside the flame, *i.e.* on the arrangement of the method of combustion. This has already been illustrated in the cases of oxygen and hydrogen (p. 113) and of hydrogen and chlorine (p. 154). Another experiment is as follows.

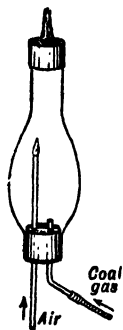


FIG. 175 — Air burning in coal gas.

A lamp chimney (Fig. 175) is fitted with a cork at the lower end through which pass a wide straight tube and a narrow tube bent at an angle. Coal gas is passed in through the bent tube and may be kindled at the top of the glass (which is covered with a piece of tin, or better a brass cap, with a central hole) where the gas burns with a luminous flame. At the same time air is drawn in through the wide tube and if a lighted taper is passed up through this tube into the chimney, the air kindles and burns in the coal gas with a blue non-luminous flame. A taper passed down to the air-flame cannot be kindled, since it is surrounded by an atmosphere of coal gas which will not support combustion of the hydrocarbons of the taper. A jet of air, however, may be ignited.

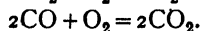
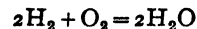


FIG. 174.—Hydrogen or carbon monoxide flame (two cones).

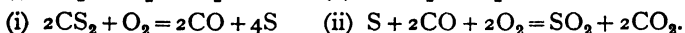
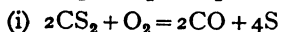
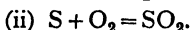
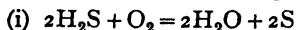
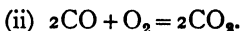
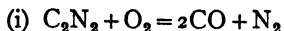
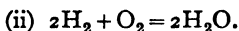
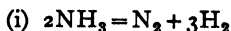


FIG. 176.—Ammonia or cyanogen flame (three cones).

The structure of flame.—(a) A hydrogen or carbon monoxide flame consists of *two* cones, an inner cone of unburnt gas and an outer cone in which a single *overall* reaction is occurring :



(b) The flames of ammonia burning in oxygen and of hydrogen sulphide, carbon disulphide vapour and cyanogen in air, consist of *three* parts (Fig. 176) corresponding with a double overall reaction outside the inner cone of unburnt gas (the actual reactions are more complex) :



(c) A candle or coal gas flame consists of *four* parts (Fig. 177) : (a) the dark inner cone of unburnt gas or vapour of partly decomposed wax ; (b) a yellowish-white brightly luminous region occupying most of the flame ; (c) often omitted in descriptions, a small bright blue region at

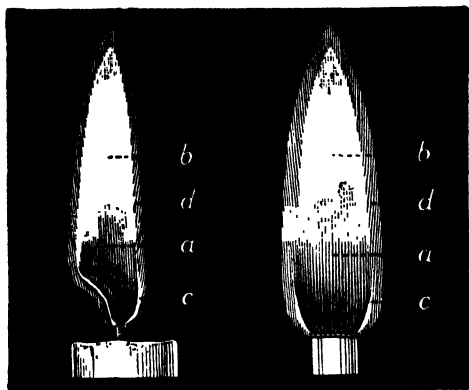


FIG. 177.—Luminous hydrocarbon flames.

the base of the flame ; (d) a faintly luminous outer mantle surrounding the flame completely. If the supply of gas is reduced the flame shrinks down, the luminous area *b* gradually disappearing whilst the region *c* becomes continuous and constitutes an inner cone. The regions *a* and *d* remain.

The structure of a candle flame is shown by Faraday's experiment.

A bent glass siphon is lowered into the flame (Fig. 178). With the tube just above the wick, dense white vapours pass over into the flask: these are formed by the volatilisation of the solid wax by the heat, which occurs on the wick at the outer edge of the dark central portion of the flame. On raising the tube into the bright central portion of the flame, steam and dense black vapours pass over, containing particles of solid carbon produced by the decomposition of hydrocarbons by the heat of the flame. With the tube at the tip of the flame, steam and carbon dioxide pass over, the gas turning lime water milky.

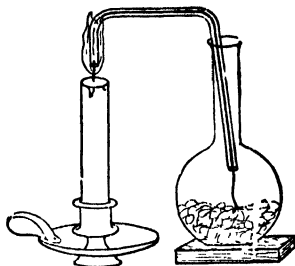


FIG. 178.—Faraday's experiment.

Davy's investigations on flame.—Sir Humphry Davy in 1815 was led to the study of flame by working on the causes and prevention of fire-damp explosions in coal mines, which were prevalent when open candle flames were used. These are caused by the ignition of mixtures of methane (*fire-damp*) and air, or as we now know, sometimes by the kindling of a mixture of very fine coal dust itself with air. Davy made the discovery that if a flame is cooled it is extinguished, and he recognised that different combustible gases have different **ignition points**. The ignition point of methane is rather high, so that it is not kindled by red-hot metal.

If a piece of fine wire gauze is lowered over a bunsen flame, this at first does not pass through the gauze, owing to the cooling effect caused by conduction of heat through the metal, and a red-hot ring is seen with a dark patch in the centre corresponding with the unburnt gas. If the gauze is held long enough on the flame the temperature of the metal rises to the ignition point of this gas, which ignites and burns above the gauze.

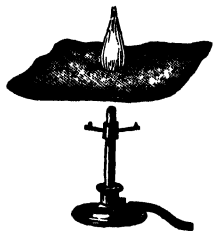


FIG. 179.—Principle of safety lamp.

If a piece of gauze turned up at the edges is held over an unlighted gas burner, the gas passing through may be kindled above the gauze but the flame does not pass through. On raising the gauze the flame flickers and finally goes out (Fig. 179). This flame, in which air is mixed with gas before combustion, is blue and non-luminous.

These experiments led Davy to the invention of the **safety lamp**, which is an oil lamp with a closed cylinder of wire gauze round the flame

(Fig. 180). Fire-damp will penetrate inside the gauze and burn there, but the flame does not pass to the gas outside because the heat is conducted away by the metal gauze. The gauze may become red-hot but

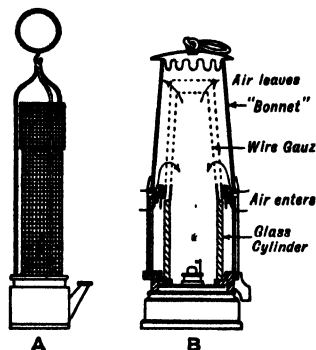


FIG. 180.—Davy lamp.

the ignition temperature of methane is high and the flame does not pass through. A strong draught of air blowing on the lamp may cause part of the gauze to become locally hot enough to kindle the fire-damp, and the flame inside may also be blown mechanically outside the gauze by a blast of air caused by a blown-out shot in a mine.

The luminosity of flame.—The luminosity of *hydrocarbon* flames was explained by Davy as due to “the decomposition of a part of the gas towards the interior of the flame, where the air was in smallest quantity, and

the deposition of solid charcoal, which first by its ignition, and afterwards by its combustion, increases to a high degree the intensity of the light”. The presence of such incandescent *solid* particles of carbon in the flame was proved by Soret, who showed that intense sunlight scattered by a luminous flame is polarised. Davy’s words (quoted above) were misunderstood to mean that the carbon was separated by a preferential combustion of hydrogen, which burnt before the carbon, but Dalton in 1810 had already proved that in the combustion of a mixture of a hydrocarbon gas with insufficient oxygen the carbon and not the hydrogen burns preferentially (pp. 398, 400), and Davy’s theory of thermal decomposition seems more correct.

Some luminous flames, however (*e.g.* of arsenic in oxygen), cannot contain solid particles.

Clouds of soot evolved from burning camphor if admitted to the lower part of a bunsen flame through one air-hole by means of a funnel tube (Fig. 181), render the flame luminous.

The theory of hydrocarbon combustion due to H. E. Armstrong and W. A. Bone assumes that the hydrocarbon is “hydroxylated” and passes through several intermediate states of oxidation, most of which can be recognised experimentally in slow combustions :

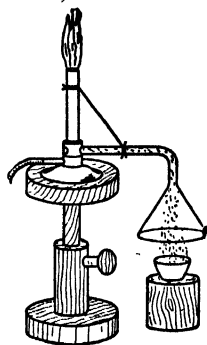
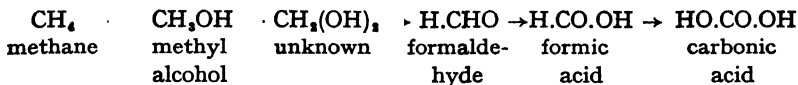


FIG. 181. — Bunsen flame rendered luminous by smoke from burning camphor.



The bunsen flame.—When coal gas is mixed with sufficient air *before* combustion it burns with a non-luminous flame as in the familiar bunsen burner (R. Bunsen, 1853). This has a small jet bringing in a stream of coal gas, over which is a wider metal tube with an adjustable hole opposite the inner jet. The coal gas passing out of the jet causes a reduction of pressure, so that air streams in through the hole in the outer tube and mixes with the gas. The mixture burns at the top of the tube. The flame consists of: (1) a pale-blue inner cone which becomes green when a large supply of air is admitted and the flame “roars”; (2) a paler-blue outer cone. The reactions in the inner cone are different from the thermal decompositions taking place in an ordinary flame, since partial oxidation now occurs with the formation of carbon monoxide which burns in the outer cone.

The two cones may be separated by Smithells' apparatus. This consists (Fig. 182) of a glass tube sliding inside a wider tube. A strip of copper foil is bound with wire to the top of each tube. A mixture of air and gas from a bunsen burner is passed into the central tube and kindled at the top. By raising the outer tube the flame at the top separates into two cones, one of which remains on the outer tube and the other, which is the inner cone of the complete flame, burns on the top of the narrower tube. By raising the latter the inner cone may be joined to the outer one and the complete flame produced. The inner cone may also be made to drop to the lowered inner tube by increasing the air-supply to the burner.

The bunsen burner is used in everyday appliances making use of gas. Its only drawback is the tendency to “strike back” when the supply of gas is too small. The rate of supply must be sufficient to stop the combustion (which travels through the mixture of air and gas at a certain rate) from running down the tube and kindling the undiluted gas at the small jet, causing the burner to become very hot and also producing incompletely burnt gas with an unpleasant odour (p. 401). The striking back may be prevented by covering the top of the burner with metal gauze, through which the flame cannot pass, as

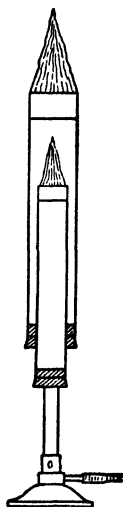


FIG. 182.—Smithells' apparatus.

is done in modern gas stoves. In gas furnaces, a blowpipe type of burner is often used, consisting of two concentric metal tubes (Fig. 113), the air being supplied under pressure through the inner tube. The mechanical action of the blast causes better thermal contact with the object to be heated.

Explosion and detonation.—A mixture of inflammable gas with oxygen or air when kindled burns with great rapidity and in an open vessel there is usually a report called an "explosion". Berthelot, Dixon and others found that an explosion *starts* with less violence and the flame runs through the gas at first with a fairly low speed. At a certain point the speed suddenly increases enormously and a flame rushes through the gas in the form of a **detonation wave**, travelling with great velocity and capable of exerting great destructive action.

In gas or petrol engines a compressed mixture of gaseous or "atomised" fuel and air is ignited in the cylinder by an electric spark. The burning produces a high temperature and a rise of pressure which drives the piston down the cylinder. In the Diesel engine the ignition is brought about by the high temperature produced by compression of the air in the cylinder, oil being then sprayed into the heated air.

The normal process of combustion in the engine cylinder is *not an explosion* in the usual sense but is a *rapid burning* of the mixture, with the production of a high temperature and pressure rise. When true detonation sets in a peculiar rattling noise known as "pinking" or detonation begins, and this is detrimental.

The formation of a detonation wave may be shown in the following experiment. A glass tube about 5 ft. long and $1\frac{1}{2}$ in. diam. is corked at one end, and filled with nitric oxide over water. The water is allowed to drain from the tube, and a cork inserted in the open end whilst it is under water. The tube is then uncorked at one end and a few c.c. (too much is detrimental) of carbon disulphide poured in, the cork being inserted quickly. The tube is tilted a few times to evaporate the carbon disulphide (when the corks tend to blow out) and is fixed vertically in a clamp. The upper cork is taken out and the gas kindled with a taper. A beautiful blue flame runs down the tube, at first quietly but finally very rapidly and with a peculiar "howling" noise as the detonation wave begins.

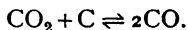
Dangerous explosions (detonations) may also be caused by the ignition of fine combustible dust dispersed in air. For example, very bad explosions have been caused in collieries by fine coal dust, and in flour mills by fine flour dust. In "dusty" mines powdered stone ("incombustible dust") is laid down; it becomes stirred up by a disturbance and damps out the explosion which might be caused by ignition of the coal dust and air.

CARBON MONOXIDE

History.—A combustible gas which he distinguished by the colour of its flame from common inflammable air [hydrogen] was obtained by Priestley in 1772; in 1776 Lassone obtained it by strongly heating zinc oxide with charcoal. This gas was confused with hydrogen until Cruickshank in 1800 found by exploding with oxygen that it was an oxide of carbon containing less oxygen than carbon dioxide. The composition was more accurately determined by Clement and Desormes in 1802, who also found that it is formed when carbon dioxide is passed over red-hot charcoal. The gas is sometimes called *carbonic oxide* (cf. *nitric oxide* NO).

Preparation.—Above a clear fire are seen flickering blue flames due to carbon monoxide CO, burning to carbon dioxide.

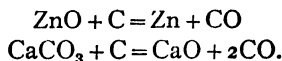
The formation of carbon monoxide in a fire is usually explained by the reduction of carbon dioxide, produced in the lower part of the fire in presence of the free air, to monoxide in passing through the mass of incandescent carbon in the centre of the fire. Carbon monoxide is in fact produced when a slow stream of carbon dioxide is passed through a *strongly* heated tube packed with charcoal:



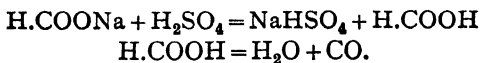
The gas from the tube contains both carbon dioxide and carbon monoxide, since an equilibrium is set up; by passing through soda-lime the carbon dioxide is removed.

Some chemists consider that carbon monoxide is a *primary* product of the combustion of carbon (p. 386): $2\text{C} + \text{O}_2 = 2\text{CO}$.

Carbon monoxide is also produced by strongly heating the oxides of zinc, iron or manganese with charcoal, or charcoal with chalk (calcium carbonate) or barium carbonate:



None of these methods is suitable for the laboratory preparation of carbon monoxide. In the laboratory preparation concentrated sulphuric acid is dropped into liquid formic acid H.CO.OH, or (more conveniently) on solid sodium formate:



The sulphuric acid “abstracts the elements of water” from the formic acid, pure carbon monoxide is evolved and may be collected over water. It may be dried by sulphuric acid, calcium chloride, or phosphorus pentoxide, and collected over mercury.

Great care must be exercised in all experiments with carbon monoxide, as it is very poisonous.

Crystals of oxalic acid on warming with concentrated sulphuric acid evolve a mixture of equal volumes of carbon monoxide and carbon dioxide. On passing the gas through a solution of sodium hydroxide in a wash-bottle the carbon dioxide is removed and the carbon monoxide may be collected :



Potassium ferrocyanide on heating in a large flask with concentrated sulphuric acid evolves carbon monoxide rather violently :



Properties.—Carbon monoxide is a colourless gas with a peculiar faint smell. It is *very poisonous*, being absorbed by the haemoglobin of the blood to form a very stable bright-red carboxyhaemoglobin, thus displacing oxygen from the blood and preventing it from combining with haemoglobin and so reaching the tissues. Many deaths have been caused by the carbon monoxide present in coal gas, in gas from coke and charcoal fires, and in the exhaust gas from motor engines ; sudden weakness prevents the escape of the victim. A bright-red colour of the face is characteristic of poisoning by carbon monoxide.

One volume of carbon monoxide in 800 volumes of air is fatal when breathed for half an hour, and even 1 vol. in 100,000 of air is said to produce unpleasant effects when breathed for some time.

The "after damp" (German, *dampf* = vapour) formed in coal mines after an explosion of fire-damp (methane, see p. 398) owes its poisonous properties to carbon monoxide (not dioxide, as was formerly supposed). Birds and mice are extremely sensitive to this gas and miners in rescue parties generally take down canaries in cages to give warning of its presence. The compound of carbon monoxide and chlorine, **carbonyl chloride** or *phosgene* COCl_2 , is also a very poisonous gas and was largely used in chemical warfare.

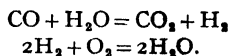
Carbon monoxide is liquefied with much greater difficulty than carbon dioxide (*cf.* NO and NO_2) ; it is sparingly soluble in water but is absorbed by a solution of cuprous chloride in hydrochloric acid or in ammonia, which may be used to separate it from other gases. Carbon monoxide forms compounds called **carbonyls** with some metals, *e.g.* nickel carbonyl $\text{Ni}(\text{CO})_4$ and iron carbonyls, $\text{Fe}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2(\text{CO})_9$. These are usually volatile liquids.

Carbon monoxide is a stable gas, not decomposed at high temperatures. It is a neutral oxide but is absorbed by hot sodium hydroxide (or soda-lime) to

produce sodium formate : $\text{NaOH} + \text{CO} = \text{H.CO.ONa}$, thus behaving as the anhydride of formic acid (from which it is produced by withdrawal of water).

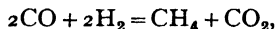
Carbon monoxide is a combustible gas, burning in air or oxygen with a beautiful blue flame to produce carbon dioxide : $2\text{CO} + \text{O}_2 = 2\text{CO}_2$. A mixture of carbon monoxide and oxygen is explosive but not so violently in small quantities as the hydrogen-oxygen mixture.

Dixon in 1880 made the interesting discovery that a CO-oxygen mixture dried by phosphorus pentoxide cannot be exploded by an electric spark, and Traube in 1885 that a flame of dry carbon monoxide burning in ordinary moist air is extinguished when introduced into a bottle of air dried by standing in contact with concentrated sulphuric acid. Dixon explained the catalytic action of water vapour by supposing that the carbonic oxide is really burnt by the steam :

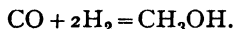


Lothar Meyer and Dixon already knew that slow combination without explosion occurs when electric sparks are passed through a *dry* CO-oxygen mixture, and Bone in 1926 found that such a mixture can be exploded by a very powerful spark, although burning is not complete.

When a mixture of carbon monoxide and hydrogen is passed over nickel at 380° , methane and carbon dioxide are formed :

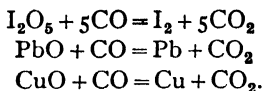


but in presence of zinc oxide (with some chromium oxide) at 350° and at high pressures methyl alcohol is produced :



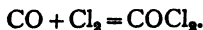
Large quantities of methyl alcohol are made in this way.

Carbon monoxide is a good *reducing agent*. It reduces iodine pentoxide and heated metallic oxides :



This property is used in the extraction of metals from ores, the carbon of the fuel (*e.g.* coke) being first converted into monoxide by a limited supply of air and the monoxide then reduces the heated oxide of the metal (*e.g.* in iron smelting in the blast furnace). Gases containing carbon monoxide are also used as fuels (see below).

Carbon monoxide combines directly with chlorine in presence of sunlight or of charcoal to form carbonyl chloride :



A mixture of carbon monoxide and sulphur vapour when passed through a heated tube forms gaseous **carbonyl sulphide** : $\text{CO} + \text{S} = \text{COS}$.

The *formula* of carbon monoxide may be found by exploding a mixture of 2 vols. of the moist gas with 1 vol. of oxygen in a eudiometer, when 2 vols. of carbon dioxide are formed (absorbable by potash). It follows that 2 molecules of carbon monoxide and 1 molecule of oxygen form 2 molecules of carbon dioxide or 1 molecule of carbon monoxide and $\frac{1}{2}$ molecule (1 atom) of oxygen give 1 molecule of carbon dioxide. The formula of carbon dioxide is CO_2 , and since this is formed from 1 molecule of the monoxide and 1 atom of oxygen, the formula of carbon monoxide must be CO. This is *confirmed* by the density, which shows that the molecular weight is 28.

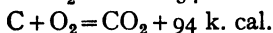
The gravimetric composition may be found by passing a measured volume of the gas (of known density) in a slow stream over red-hot copper oxide and absorbing the carbon dioxide produced in weighed soda-lime tubes. If the composition of carbon dioxide is known that of the monoxide may be calculated from the result.

The structural formula of carbon monoxide is $\text{C}\equiv\text{O}$ corresponding with the electronic formula $\times \text{C} \times \times \text{O} :$ (see p. 264B).

FUEL GASES

Two types of fuel gas made from carbon are producer gas and water gas.

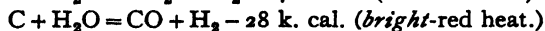
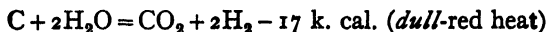
Producer gas is a mixture of carbon monoxide, carbon dioxide and nitrogen obtained by passing air through a large mass of incandescent coke in an upright cylindrical furnace called a **gas producer** :



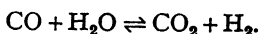
The overall reaction is *exothermic* and the process can go on continuously if the fuel is renewed. The hot gas is then burnt where it is required by admitting a further quantity of air, when the monoxide burns to carbon dioxide.

The ratio CO/CO_2 in the gas increases with the temperature of the red-hot carbon. The gas from coke always contains some sulphur dioxide, from sulphur compounds in the coke.

Water gas is a mixture of carbon monoxide, hydrogen, and some carbon dioxide, obtained by passing steam through incandescent coke. This reaction absorbs heat or is *endothermic*, so that (unlike the formation of producer gas, which is exothermic) the formation of water gas must be frequently stopped and the fuel brought to a high temperature again by blowing air through it. Two reactions between carbon and steam occur in the making of water gas :



Actually, both reactions always take place together, since in presence of steam carbon monoxide is partly converted into dioxide by the reversible "water-gas reaction":



The ratio CO/CO_2 in water gas increases with the temperature. The equilibrium constant

$$\frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = K$$

increases from about 1.5 at 1000° to about 2.5 at 1500° .

The volume compositions of typical fuel gases are :

		H_2	CO	CO_2	N_2	CH_4	H_2S
Producer gas	-	18.7	26	6	49	0.3	—
Water gas	-	52	40	4.5	2.1	0.8	0.6

Water gas burns with a blue non-luminous flame and is generally added to coal gas, since it has a good calorific power. To increase the illuminating power when burnt from common burners, the "blue" water gas (burning with a blue flame) is "carburetted" by passing it through hot brickwork over which oil is sprayed.

In the apparatus shown in Fig. 183 the water gas is made in the gas producer on the left by blowing steam through red-hot coke. The hot

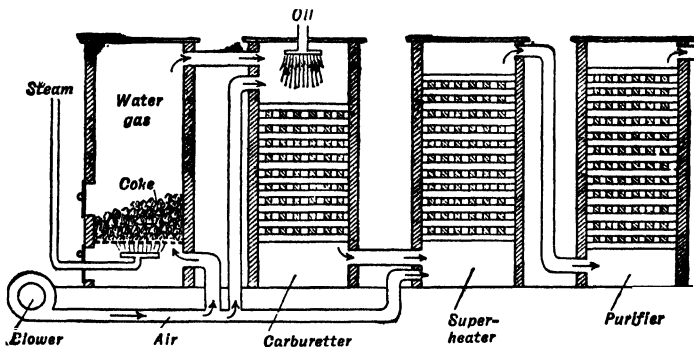


FIG. 183. —The manufacture of carburetted water gas.

gas then passes through a tower (called the carburettor) packed with heated bricks and a spray of oil is injected. The oil is converted into vapour, which is then decomposed ("cracked") by heating and gaseous hydrocarbons such as ethylene, which burn with a luminous flame, are formed. This process occurs in the superheater, which is a tower packed with bricks previously made red-hot by the combustion of a mixture of producer gas and air. The carburetted water gas then passes to the purifier where hydrogen sulphide (from sulphur in the coke) is taken out.

When the coke in the producer has cooled down, the steam is shut off and air is blown through to raise the temperature of the coke. This

forms producer gas, which passes through the carburetter, heating the bricks, and then into the superheater where it is mixed with air and burns, so heating the bricks. The products of combustion go to waste.

The volume composition of a typical carburetted water gas is $H_2 = 40$, $CO = 30$, saturated hydrocarbons = 16, unsaturated hydrocarbons = 7, nitrogen = 6.8, oxygen = 0.2.

When incandescent gas mantles are used the illuminating power of gas is of little importance, and modern coal gas, which is frequently mixed with water gas, is sold on its calorific or heating value in therms.

The *Welsbach mantle* is a tissue of 99 per cent. of thorium oxide or *thoria* ThO_2 , and 1 per cent. of cerium dioxide or *ceria* CeO_2 , both oxides being obtained from the *monazite sand* found in India. Pure thoria gives out only a feeble light when strongly heated, but when mixed with 1 per cent. of ceria it glows brightly.

The old type of mantle consisted of ramie-fibre cellulose soaked in a solution of thorium and cerium nitrates, to which some beryllium nitrate was added to confer toughness. The whole was burnt off to form an oxide skeleton, which was impregnated with collodion to confer rigidity, the collodion being burnt off just before use. The modern soft mantles are of artificial silk impregnated with the nitrates and are not burnt off or collodionised before sale.

CARBON DIOXIDE

History.—Carbon dioxide, called *gas sylvestre* by Van Helmont about 1630, was studied by Black (1754), who called it *fixed air*, and more carefully in 1774 by Bergman, who showed that it was weakly acidic. Lavoisier in 1783 showed that it was an oxide of carbon and determined its composition by burning charcoal in oxygen. He called it *carbonic acid gas* because it is an acidic oxide, forming with basic oxides salts called *carbonates*.

Occurrence.—Carbon dioxide issues in abundance from the earth in certain localities such as the Poison Valley (Java) and the Grotto del Cane (Naples). It occurs in many mineral waters such as those of Selters and Vichy. By the combustion of carbonaceous fuels large quantities of carbon dioxide pass into the atmosphere, which contains about 3 volumes of carbon dioxide in 10,000. Carbon dioxide is formed during respiration, as may be shown by blowing expired air through lime-water, which becomes turbid owing to the precipitation of calcium carbonate. The fermentation of sugar in the preparation of beer and wine produces carbon dioxide and alcohol :



Other kinds of fermentation and the decay of organic matter also produce carbon dioxide, so that it is evolved from the soil.

Carbon dioxide is removed from the atmosphere in the "weathering" of rocks such as felspar, when soluble alkali carbonates are formed and retained by the soil (p. 372). It is also removed by green plants in photosynthesis (p. 428) :



The carbon of plant remains is partly stored in coal beds.

Carbon dioxide dissolved in the sea forms calcium bicarbonate, which is utilised by marine organisms, which retain half the carbon as normal carbonate and set free the other half as carbon dioxide. When the organisms die the calcium carbonate is deposited in the form of chalk beds or coral reefs, which store carbon in a combined form.

As a result of all these processes the atmospheric carbon dioxide remains nearly constant, although it is probably slowly increasing. The volumes emitted by fuel combustion, lime burning, etc., are enormous, but owing to the vast extent of the atmosphere they have little effect on its composition.

Preparation.—Carbon dioxide is formed by the combustion of carbon or carbon monoxide in oxygen but is usually *prepared* by the action of acids on carbonates. Broken marble and dilute hydrochloric acid are best, and may be charged into a flask, Woulfe's bottle or Kipp's apparatus :

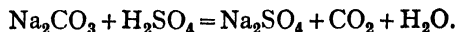


Dilute sulphuric acid should not be used with marble, since the sparingly soluble calcium sulphate produced coats the marble and soon stops the action of the acid. It acts fairly easily on powdered chalk. The gas is collected by downward displacement, since it is soluble in its own volume of water and is $1\frac{1}{2}$ times as heavy as air. It may be washed with water and dried by sulphuric acid, calcium chloride, or phosphorus pentoxide.

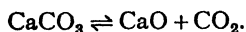
Pure carbon dioxide is obtained by heating pure sodium bicarbonate :



or by the action of dilute sulphuric acid (boiled to expel air) on pure sodium carbonate :



Carbon dioxide is evolved on heating carbonates except the normal carbonates of the alkali metals and barium carbonate, *e.g.* chalk, limestone, marble, *magnesia alba*, etc., at a red heat, and is therefore produced in lime burning :



Baking powder contains sodium bicarbonate and tartaric acid, which do not react when dry. In presence of water sodium tartrate is formed

and carbon dioxide is evolved, the bubbles of which are expanded by heat on baking :



Health salt is a similar mixture. The fermentation produced by yeast in the baking of bread forms carbon dioxide, which gives the dough a spongy texture. Sodium bicarbonate alone and ammonium carbonate, which evolve bubbles of carbon dioxide on heating, are also used in baking.

Properties.—Carbon dioxide is a colourless gas with a faint pungent smell and an acid taste. It is $1\frac{1}{2}$ times as heavy as air. Carbon dioxide extinguishes a burning taper, sulphur, phosphorus, etc. ; air containing $2\frac{1}{2}$ per cent. by volume of carbon dioxide ceases to support the combustion of a candle, although $17\frac{1}{2}$ per cent. of oxygen is still present. The gas is therefore used in extinguishing fires. A little benzene burning in a porcelain dish is at once extinguished by the heavy carbon dioxide decanted upon it from a large jar.

Fire extinguishers (Fig. 184) consist of a strong metal vessel containing a solution of sodium carbonate with a glass bottle of sulphuric acid inside.

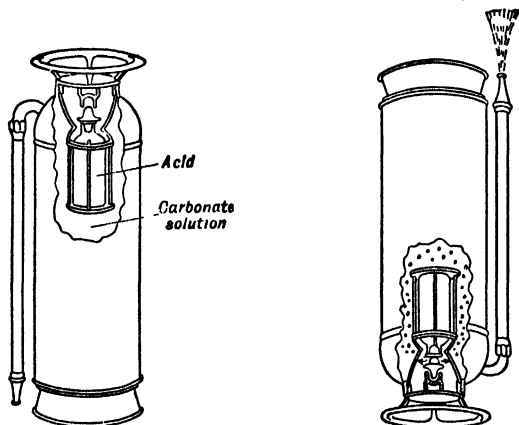


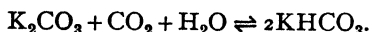
FIG. 184.—Carbon dioxide fire extinguisher.

By means of a rod attached to a knob outside the bottle may be broken, or the bottle may be inverted by tilting the extinguisher so as to pour the acid into the carbonate solution. The mixture of liquid and gas then issues forcibly from the nozzle.

For extinguishing oil and petrol fires, *firefoam* is used. This is a froth of bubbles of carbon dioxide which floats on the burning oil, and is produced by mixing a solution of sodium carbonate containing liquorice (which causes foaming) with alum. Water alone sinks in burning oil and is almost useless.

Another (*Pyrene*) type of extinguisher contains liquid carbon tetrachloride and a pump for spraying it on the fire. The heavy vapour excludes air and the fire goes out. In a strong wind it is not so effective.

Carbon dioxide is made on the large scale from marble or dolomite and acid and is purified by washing with water. It is also made by burning coke in air, washing the gas with water and absorbing the carbon dioxide in a solution of potassium carbonate; on heating the solution of bicarbonate so formed carbon dioxide is evolved:



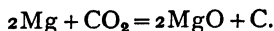
It is also obtained as a by-product in making hydrogen from water gas (p. 132) and in alcoholic fermentation.

Carbon dioxide is liquefied without much difficulty by compression provided the temperature is below its critical temperature of 31° . The *liquid* is sold in large steel cylinders from which the gas may be taken by standing the cylinder upright with the valve above. If the cylinder is laid on its side and the valve opened, a jet of liquid carbon dioxide issues from it which, owing to further cooling by rapid evaporation, at once freezes to a snow-like *solid* which may be collected by firmly tying a canvas bag to the jet. The solid may be handled with a horn spoon; if pressed between the fingers it produces painful blisters. Mercury is rapidly frozen in a mixture of solid carbon dioxide and ether (-78°C.). Compressed solid carbon dioxide is also manufactured and is called "dry ice" since it does not melt to water, as ice does, but evaporates.

Carbon dioxide gas does not support respiration and animals die in it from suffocation, but it is not poisonous. The presence of the gas in cellars, wells, etc., is easily detected by the extinction of a lighted taper which occurs with a proportion much smaller than any amount dangerous in respiration.

Carbon dioxide stimulates breathing and is mixed with oxygen in administering ether as an anaesthetic; it is used to revive respiration which has nearly ceased in cases of drowning, suffocation and shock.

Burning magnesium ribbon continues to burn (though rather reluctantly) * in a jar of carbon dioxide, withdrawing the oxygen from the gas and setting free the carbon:

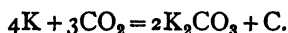


Dilute sulphuric acid dissolves the magnesia and black specks of carbon

* The ribbon burns more readily in the gas if a little air is present; stout magnesium wire burns in the undiluted gas.

are seen floating about in the liquid. In this way the presence of carbon in the gas may be demonstrated.

Heated potassium also burns in carbon dioxide :



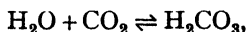
A characteristic reaction of carbon dioxide is the formation of a white precipitate of calcium or barium carbonate when the gas is passed into or shaken with lime or baryta water. The carbonate dissolves in excess of carbon dioxide to form a bicarbonate.

Sulphur dioxide also forms a white precipitate of calcium sulphite $CaSO_3$, soluble in excess to form calcium bisulphite $Ca(HSO_3)_2$, when passed into a *large* volume of lime-water. It may be separated from carbon dioxide by passing through acidified permanganate or dichromate solution.

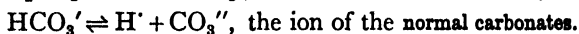
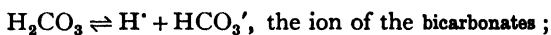
Water at room temperature dissolves about its own volume of carbon dioxide. Under pressure the solubility increases. On lowering the pressure the gas escapes with vigorous effervescence, although the liquid remains supersaturated and evolves gas slowly for some time. If the liquid is stirred or if porous solids such as sugar or bread-crumbs are thrown into it, brisk effervescence results. The whole of the carbon dioxide dissolved in water is expelled on boiling. A crystalline hydrate $CO_2 \cdot 6H_2O$ is obtained by compression and cooling.

Aerated waters (*e.g. soda water*) are charged with carbon dioxide gas under pressure. The solubility of carbon dioxide in alcohol is about twice as great as that in water.

Carbonic Acid.—The aqueous solution of carbon dioxide has a faintly acid taste and turns litmus a port wine red colour. If the amount of dissolved gas is increased by pressure, the litmus turns bright red. The liquid contains a very weak dibasic unstable carbonic acid, H_2CO_3 :



which forms two series of salts :



The dissociation constants (p. 234) at room temperature are

$$K_1 = [H^+][HCO_3'] / [H_2CO_3] = 3 \times 10^{-7} \quad K_2 = [H^+][CO_3''] / [HCO_3'] = 6 \times 10^{-11}.$$

In aqueous solution the normal carbonates react alkaline, owing to hydrolysis (p. 238) :



Formula of carbon dioxide.—The *composition of carbon dioxide by weight* is found by burning a weighed amount of pure carbon (*e.g. diamond or purified sugar charcoal*) in a small platinum or porcelain boat

X (Fig. 185) inside a hard glass tube containing a layer of copper oxide Z , which is heated to redness in a furnace. The oxygen is first passed through purifying tubes A , B containing broken sticks of

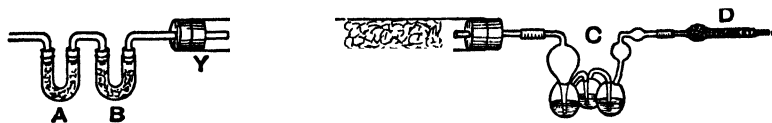


FIG. 185.—Composition of carbon dioxide by weight.

caustic potash, which remove carbon dioxide and moisture. The carbon is heated and burns. Some carbon monoxide (CO) also formed is converted into carbon dioxide by the hot copper oxide, and the carbon dioxide is collected in the bulbs C containing potash solution which, with a calcium chloride tube D to absorb moisture from the bulbs, are weighed. If x = weight of carbon, y = increase in weight of potash bulbs, then $y - x$ = weight of oxygen combined with x of carbon. It is found that 12.01 parts of carbon combine with 32 parts of oxygen.

The *formula* of carbon dioxide is found by the apparatus of Fig. 186.

The bulb contains dry oxygen over mercury and the spoon a small piece of recently ignited charcoal wrapped in a coil of very thin platinum wire attached to the stout brass terminals. On passing a current through the wire it is heated to redness and the charcoal burns in the *excess* of oxygen, producing carbon dioxide. After cooling, the volume of gas is found to be unchanged, hence *carbon dioxide contains its own volume of oxygen, i.e.* one molecule of carbon dioxide contains one molecule of oxygen and the formula is C_xO_2 .

The density of the gas shows that the molecular weight is 44. This contains one molecule of oxygen ($\text{O}_2 = 32$) and therefore $44 - 32 = 12$ parts, or one atom, of carbon. Hence the formula is CO_2 . The structural formula is $\text{O}=\text{C}=\text{O}$.

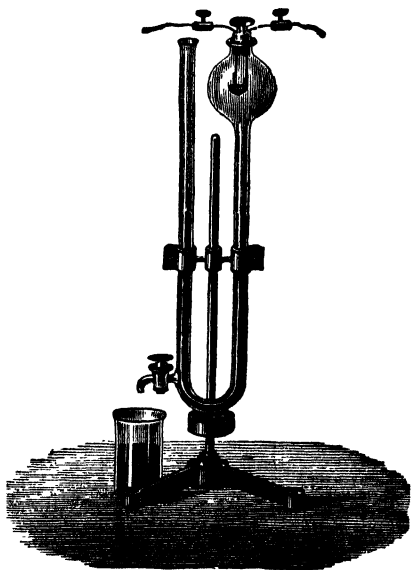


FIG. 186.—Formula of carbon dioxide.

The *atomic weight* of carbon was determined by Dumas and Stas (1841) and others by the combustion of diamond and pure graphite in oxygen and weighing the carbon dioxide. A value almost exactly 12.00 was found, after allowing for the residual ash. Richards and Hoover (1915) by neutralising hydrobromic acid with sodium carbonate and determining

the quantity of silver necessary to form silver bromide found 12.008. Owing to the existence of the isotope ^{13}C the value is higher than 12 and the limiting density of carbon monoxide (see p. 83) gives $\text{C} = 12.01$ (Gray and Woodhead, 1933).

Several kinds of **percarbonates**, such as NaHCO_4 , $\text{Na}_2\text{CO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and $\text{K}_2\text{C}_4\text{O}_8$ are formed by the electrolysis of concentrated solutions of alkali carbonates or by the action of hydrogen peroxide on these. They are oxidising agents.

The growth of plants.—Green plants contain a green pigment called *chlorophyll* which is the active agent in the decomposition of atmospheric carbon dioxide and evolution of oxygen by plants when exposed to light. The detail of the reaction, which is called *photosynthesis* because organic compounds are produced by the plant from water and carbon dioxide, is not yet sufficiently clear, but it is known that the oxygen comes from water and not carbon dioxide.

Carbon dioxide is converted in the leaves, under the action of light, into carbohydrates having the empirical formula $(\text{CH}_2\text{O})_x$, such as starch and sugar. The result may be represented by the equations :

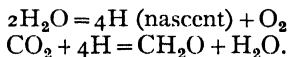


FIG. 187.—Oxygen from carbon dioxide by green plants.

The production of oxygen by living green plants under the influence of light is shown by the following experiment. Watercress, mint or (best) *Elodea canadensis*, is put into a flask filled with tap water saturated with carbon dioxide, with an arrangement for collecting gas (Fig. 187). On exposure to sunlight, bubbles of gas rise from the leaves and collect in the test-tube. These consist largely of oxygen.

Plants require oxygen for their life processes and evolve carbon dioxide. In the dark, when the photosynthesis is arrested, this respiration is the only process of gaseous exchange taking place: during the day much of this carbon dioxide may be decomposed by the chlorophyll.

Respiration.—Early experimenters such as Mayow, Scheele, Priestley and Lavoisier, were all aware of the great similarity between combustion and respiration. Lavoisier pointed out that the oxygen breathed into the lungs oxidises carbonaceous materials in the blood, producing carbon dioxide which is breathed out and that *animal heat* is the result of this chemical process of oxidation (Fig. 188). The presence of carbon dioxide in air from the lungs is easily demonstrated by blowing through a piece of glass tubing into lime-water, when a white precipitate of calcium carbonate is produced.

Lavoisier thought that oxidation with production of animal heat occurs in the lungs, but Mayow already knew that it takes place in the tissues. The blood holds in suspension corpuscles containing a red colouring matter *haemoglobin*, which absorbs one molecule of oxygen to produce a bright red substance *oxyhaemoglobin*, which exists in the blood of the arteries passing from the lungs to the tissues. In the tissues the loosely-combined oxygen is absorbed and oxidation processes occur. These are the source of animal heat and energy, and one of the products is carbon dioxide which remains in solution as carbonic acid or bicarbonates. The



FIG. 188.—Lavoisier's experiments on respiration.

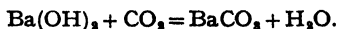
The subject is breathing air or oxygen from a jar standing in a trough through a tube fitted in a mask. Madame Lavoisier is seated at the desk.

de-oxygenated blood corpuscles now have a dark purple colour, and part of the blood containing them passes back to the heart by the veins to be pumped to the lungs for re-oxidation.

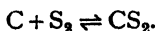
In consequence of the activities of plants and animals, the plants absorbing carbon dioxide from the atmosphere, retaining the carbon and liberating the oxygen, and the animals absorbing oxygen and giving off carbon dioxide, a kind of *balance* is maintained in the ratio of oxygen and carbon dioxide in atmospheric air. Carbon dioxide is fairly soluble in water and is also dissolved by the sea from the atmosphere.

Normal outdoor air contains about 3 volumes of carbon dioxide per 10,000. In crowded rooms not sufficiently ventilated, the proportion of carbon dioxide may rise to 0.04 to 0.3 per cent. by volume. The "stuffiness" and bad effects of breathed air are due to moisture and organic matter and not to carbon dioxide.

The amount of carbon dioxide is determined by **Pettenkofer's method** : a measured volume of standard baryta solution is shaken with a known large volume (8 to 10 lit.) of air in a stoppered bottle, and the excess of baryta left is titrated with standard acid and phenolphthalein :



Carbon disulphide.—Carbon disulphide was discovered in 1796 by Lampadius by heating pyrites with charcoal. Clement and Desormes in 1802 showed that it is formed when sulphur vapour is passed over red-hot carbon. The reaction takes place between carbon and S_2 molecules in the sulphur vapour, and is reversible :



A vertical cast-iron or fire-clay retort set in a furnace is filled with charcoal. Sulphur is fed in through a side tube at the base of the retort, being kept fused by the waste heat. The sulphur vapour passes over the red-hot charcoal, forming carbon disulphide. The vapours pass through a small iron cylinder, where sulphur is deposited, and the carbon disulphide is condensed in a very long worm-tube cooled by water. In Taylor's process, used in America, electric heating is used but a very high temperature is not necessary.

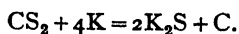
Carbon disulphide is purified by distillation over lead acetate, or by agitation with mercury until it no longer blackens it, after which it is redistilled over white wax and then over phosphorus pentoxide.

Carbon disulphide is a colourless, mobile, strongly refracting liquid, which boils at 46° . It is almost insoluble in water but mixes with absolute alcohol, ether, and oils. It dissolves sulphur, white phosphorus, india-rubber, camphor, resins, etc., and is used as a solvent. Carbon disulphide is very volatile. Its vapour has usually an exceedingly unpleasant odour which is removed by careful purification, when the liquid smells of chloroform, but the smell soon becomes unpleasant again. Carbon disulphide vapour is a powerful poison for moths in furs, etc., and mice and rats in grain elevators.

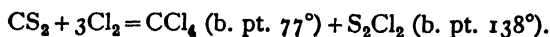
The vapour has a low ignition temperature and a test-tube filled with hot oil sets fire to it. A mixture of the vapour with air or oxygen explodes when kindled, the most violent explosion being obtained with $2\text{CS}_2 + 5\text{O}_2 = 2\text{CO} + 4\text{SO}_2$. Sulphur trioxide and carbon dioxide are also formed.

Carbon disulphide, being endothermic with reference to solid carbon and sulphur, is unstable. If a little mercury fulminate is exploded in a tube filled with the vapour, decomposition commences with separation of sulphur and carbon but is not propagated through the vapour.

Carbon disulphide vapour is decomposed by heated potassium :



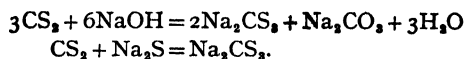
When chlorine is passed into boiling carbon disulphide containing a little iodine, carbon tetrachloride is formed :



Both products of this reaction are useful and are separated by fractional distillation. Carbon tetrachloride is used as a grease solvent, and under the name of *pyrene* (p. 425) for extinguishing fires (*not sodium*!). When carbon tetrachloride is heated with fuming sulphuric acid, pyrosulphuryl chloride is formed and carbonyl chloride (*phosgene*) gas is evolved :



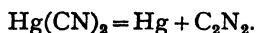
Carbon disulphide dissolves in a concentrated solution of an alkali hydroxide, or more easily in an alkali sulphide, a thiocarbonate being formed :



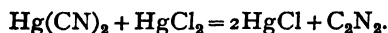
CS_2 thus behaves as the thioanhydride of thiocarbonic acid H_2CS_3 , just as CO_2 is the anhydride of carbonic acid H_2CO_3 . Thiocarbonic acid is an oily liquid formed by the action of an acid on a thiocarbonate.

Cyanogen.—By heating mercuric cyanide Gay-Lussac in 1815 obtained a gas which burns with a peach-blossom coloured flame. This is cyanogen, C_2N_2 .

Cyanogen, *which is very poisonous*, is produced by heating the cyanides of silver, mercury and gold, the most convenient being mercuric cyanide, which is heated to dull redness in a hard glass or steel tube :



A heavy brown non-volatile powder called *paracyanogen* produced at the same time is probably a polymerised form of cyanogen $(\text{CN})_x$. The gas is evolved at a lower temperature if mercuric chloride is mixed with the cyanide :



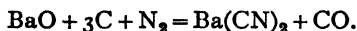
An economical method for the preparation of cyanogen (which is not pure, but contains some carbon dioxide and hydrocyanic acid) is to drop a concentrated solution of potassium cyanide into a warm solution of 2 parts of crystallised copper sulphate in 4 parts of water. Cupric cyanide $\text{Cu}(\text{CN})_2$ is first formed as a yellow precipitate but quickly decomposes with evolution of cyanogen gas, forming white cuprous cyanide CuCN :



If the cuprous cyanide is filtered off and heated with ferric chloride solution, the rest of the cyanogen is evolved :



Cyanides are produced by the action of nitrogen on carbides at high temperatures : if nitrogen is passed over barium carbide or an intimate mixture of barium oxide and carbon at a red heat, barium cyanide is produced :



Cyanogen is present in small quantities in blast-furnace gas.

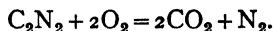
Cyanogen is a colourless gas soluble in water and must be collected over mercury. It has a smell of bitter almonds and is *very poisonous*. When cooled it condenses to a colourless liquid. The density of the gas shows that it has the formula C_2N_2 . It is an endothermic compound. Cyanogen combines with halogens to form gaseous cyanogen chloride CNCl , and solid cyanogen bromide CNBr and cyanogen iodide CNI .

Cyanogen is absorbed by a solution of potassium hydroxide forming potassium cyanide KCN and potassium cyanate KCNO :

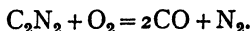


In this reaction, cyanogen resembles chlorine. Since all cyanogen compounds contain the univalent cyanogen group or radical CN , the latter is sometimes written Cy since it behaves to some degree as an element. In solutions of cyanides the cyanide ion CN' is formed : $\text{KCN} = \text{K}' + \text{CN}'$.

Cyanogen gas burns when kindled in air or oxygen with a beautiful peach-blossom coloured flame (p. 412) :



A mixture of equal volumes of cyanogen and oxygen explodes when sparked even when carefully dried over phosphorus pentoxide, with the production of carbon monoxide and nitrogen :



With double the volume of oxygen, the monoxide is burnt to carbon dioxide.

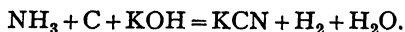
1 vol. of cyanogen when exploded with 2 vols. of oxygen gives 2 vols. of carbon dioxide (absorbed by potash) and 1 vol. of nitrogen. It follows that the molecule of cyanogen contains 2 atoms of carbon and 2 atoms of nitrogen, and the formula C_2N_2 may be confirmed by the density. The structural formula is $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$.

Hydrocyanic acid.—Hydrocyanic acid (or *prussic acid*) HCN was discovered by Scheele in 1782 by distilling potassium ferrocyanide with

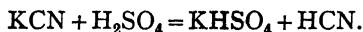
dilute sulphuric acid, when a dilute solution of hydrocyanic acid distils over (*poisonous* !):



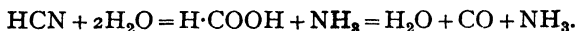
Scheele also found that potassium cyanide is formed when ammonia gas is passed over a heated mixture of potash and charcoal:



When potassium cyanide is distilled with a mixture of equal volumes of sulphuric acid and water the vapour of hydrocyanic acid is evolved:



With *concentrated* sulphuric acid, carbon monoxide is formed:



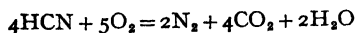
The gas is dried by calcium chloride, and when passed through a U-tube cooled in ice and salt condenses to a colourless liquid, which is anhydrous hydrocyanic acid.

The anhydrous acid is best produced by slowly passing pure hydrogen sulphide over dry mercuric cyanide heated at 30° in a long glass tube, and condensing the liquid in a freezing mixture. Hydrocyanic acid is formed when acetylene is sparked with nitrogen: $\text{C}_2\text{H}_2 + \text{N}_2 = 2\text{HCN}$, and by the action of a silent discharge on a mixture of cyanogen and hydrogen: $\text{C}_2\text{N}_2 + \text{H}_2 = 2\text{HCN}$.

Anhydrous hydrocyanic acid is a colourless mobile liquid of low boiling point (25°). Its vapour burns in air with a purple flame. The acid has a peculiar smell difficult to describe and usually said to resemble that of crushed peach-kernels; these and also crushed laurel leaves evolve traces of hydrocyanic acid. Some persons are almost incapable of detecting the smell, which is safely tested with a bottle of potassium cyanide.

Hydrocyanic acid is a really dangerous poison; it strikes swiftly and with deadly potency and recovery from a lethal dose is rare.

The formula of hydrocyanic acid may be found by exploding a mixture of the vapour with oxygen in a eudiometer, when the reaction:



occurs: the carbon dioxide (absorbed by alkali) and the nitrogen are measured; 1 vol. gives 1 vol. of CO_2 and $\frac{1}{2}$ vol. N_2 , and from this and the volume of oxygen consumed the formula HCN follows. The structural formula is $\text{H}-\text{C}\equiv\text{N}$.

Hydrocyanic acid is a very weak acid and its salts are hydrolysed in solution: $\text{CN}' + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}'$. The solutions smell of the free acid and show an alkaline reaction.

Potassium cyanide is formed by heating potassium ferrocyanide alone at a bright-red heat :



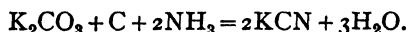
or with potassium carbonate :



If the ferrocyanide is fused with sodium a mixture of sodium and potassium cyanides is formed :

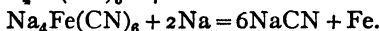
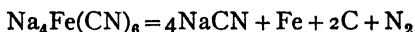


Potassium cyanide is prepared by **Beilby's process** ; dry ammonia gas is passed over a mixture of fused potassium carbonate and carbon :

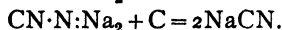
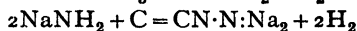
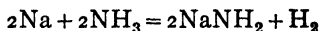


The fused cyanide is decanted and moulded, and is pure.

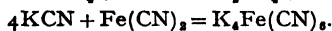
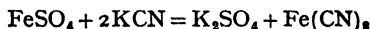
Sodium cyanide is formed by heating sodium ferrocyanide alone or with sodium :



The pure cyanide is precipitated by passing hydrocyanic acid gas into alcoholic sodium hydroxide. Sodium cyanide is made on a large scale by **Castner's process** ; dry ammonia gas is passed over sodium heated in iron retorts and the fused sodamide produced is poured over red-hot charcoal, when **sodium cyanamide** $\text{Na}_2\cdot\text{N}\cdot\text{CN}$ is first formed and then reacts with the heated charcoal to form sodium cyanide :



Tests for cyanides.—(1) A solution of a cyanide gives with silver nitrate a white curdy precipitate of **silver cyanide** AgCN , soluble in boiling concentrated nitric acid. (2) To the solution of the cyanide caustic soda is added and a few drops of a mixed solution of ferrous sulphate and ferric chloride ; on warming a **ferrocyanide** is produced :

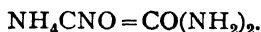


The dirty-brown precipitate is warmed with hydrochloric acid, which dissolves the ferric hydroxide and leaves dark-blue **Prussian blue**, formed by the action of the ferrocyanide on the ferric salt. If only traces of cyanides are present a blue or green colour appears. (3) The solution is evaporated to dryness on a water bath with yellow ammonium sulphide, when a **thiocyanate**, *e.g.* KCNS , is formed :

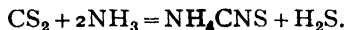


The residue is dissolved in water and ferric chloride solution is added, when a blood-red coloration of ferric thiocyanate $\text{Fe}(\text{CNS})_3$ is formed.

Fused potassium or sodium cyanide is a powerful *reducing agent*, converting metallic oxides into metal and being itself oxidised to a **cyanate** : $\text{KCN} + \text{PbO} = \text{Pb} + \text{KCNO}$. Fusion mixture containing potassium cyanide is used in blowpipe analysis, since it reduces some oxides (*e.g.* stannic oxide) not easily reduced on charcoal with ordinary fusion mixture. The cyanate formed in the above reaction may be extracted with water ; when the solution is acidified the cyanic acid first formed is very rapidly decomposed with formation of ammonia and evolution of carbon dioxide : $\text{HCNO} + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2$. (A cyanate could, therefore, be mistaken for a carbonate.) Ammonium cyanate is converted into urea when the solution is evaporated :



Thiocyanates are formed when cyanides are fused with sulphur : $\text{KCN} + \text{S} = \text{KCNS}$; or the ammonium salt on heating a mixture of carbon disulphide, concentrated ammonia and alcohol :



Ammonium thiocyanate is made in gas-works (p. 408).

Thiocyanates are decomposed by dilute acids with liberation of thiocyanic acid HCNS ; with concentrated sulphuric acid the thiocyanic acid is decomposed into ammonia (forming ammonium sulphate) and inflammable gaseous **carbonyl sulphide** : $\text{CNSH} + \text{H}_2\text{O} = \text{COS} + \text{NH}_3$.

CHAPTER XXVII

SILICON, TIN AND LEAD

SILICON

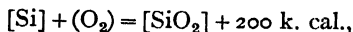
History.—Silica was at first regarded as an "earth" analogous to lime and alumina but its acidic character was pointed out by Otto Tachenius in 1666 : it is insoluble in acids but dissolves in potash forming a solution of a silicate, formerly known as *liquor of flints*. Gay-Lussac and Thenard in 1811 obtained silicon as a brown amorphous powder on passing silicon fluoride gas over heated potassium, but did not recognise its true nature. In 1823 Berzelius prepared it by heating potassium fluosilicate with potassium : $K_2SiF_6 + 4K = 6KF + Si$. He considered it to be a metal, whereas Davy from its analogy with carbon regarded it as a non-metal. In most of its properties silicon belongs to the group of non-metallic elements, although it forms alloys with metals such as copper and iron.

Occurrence.—Next to oxygen (50 per cent.) silicon (26 per cent.) is the most abundant element in the crust of the earth : it occurs as silicon dioxide or *silica* SiO_2 , varieties of which are quartz, sand, flint, etc. Silica is the acidic part of the *silicate rocks*. Granite and similar primitive rocks contain from 20 to 30 per cent. of silicon. Silica also occurs in plants and animals.

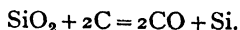
Straw and bamboo contain fairly large quantities of silica : the common "horse-tail" leaves on combustion a siliceous skeleton. The feathers of some birds contain 40 per cent. of silica which also occurs in sponges, and deposits of almost pure silica are found in the form of *kieselguhr* which consists of the siliceous skeletons of extinct *diatoms*. This very porous material is used to absorb nitroglycerin in the preparation of dynamite and in "lagging" steam pipes to retard loss of heat.

Superheated water in the interior of the earth, especially if alkaline, dissolves silica, which occurs in many spring waters, in hot-springs and particularly in the boiling water of geysers such as the Great Geyser of Iceland, the Hot Springs of New Zealand, and the Mammoth Springs of Yellowstone Park, U.S.A. The dissolved silica is deposited at the mouth of the geyser as *sinter*. Dissolved silica may also pass into the pores of wood, etc., in the earth, producing *petrification*.

Preparation.—Silicon has a great affinity for oxygen :



so that silica can be reduced only by powerful reducing agents or at high temperatures, as when heated with carbon in the electric furnace :



It is made in this way at Niagara by heating a mixture of sand and crushed coke, or by reducing silica with calcium carbide. Silica is also reduced when heated with carbon and iron in the blast furnace, and cast iron always contains silicon. Iron containing carbon and more than 15 per cent. of silicon is very resistant to acids, except hydrochloric.

In the laboratory silicon is most conveniently prepared by heating silica with magnesium powder : $\text{SiO}_2 + 2\text{Mg} = 2\text{MgO} + \text{Si}$.

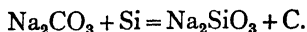
Two grams of a mixture of 5 parts of powdered quartz or *thoroughly dried* (recently ignited) amorphous silica with 3 parts of magnesium powder and 2 parts of calcined magnesia to moderate the reaction, are heated in a covered silica crucible. The mass glows when vigorous reaction occurs. After cooling the magnesia is dissolved out by hydrochloric acid and the silicon washed and dried in a steam oven. It may be purified by washing in a platinum crucible with hydrofluoric and sulphuric acids.

The silicon so prepared is usually called “amorphous” although the X-rays show that it consists of minute octahedral crystals. It is a *light* chestnut-brown powder which oxidises only superficially when heated in air but burns brilliantly to silica when heated in oxygen.

It ignites spontaneously in fluorine forming the fluoride SiF_4 , and burns when heated in chlorine with production of the tetrachloride SiCl_4 . Amorphous silicon is insoluble in water and acids except a mixture of nitric and hydrofluoric ; it is slowly attacked by steam at a red heat : $\text{Si} + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2$. A mixture of potassium chlorate and nitric acid has no action upon it (*cf.* carbon), but it dissolves readily in hot concentrated alkali hydroxide solution, or in fused sodium carbonate, potassium nitrate or potassium chlorate :

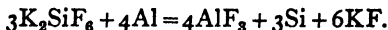


It displaces carbon when fused with sodium carbonate :



Amorphous silicon when strongly heated in a closed crucible fuses, and on cooling solidifies to the dense crystalline so-called *graphitoid silicon*, which also results from the reduction of silica in the electric furnace. Octahedral crystals of silicon, orange or black in colour, are produced by strongly heating potassium fluosilicate with sodium and

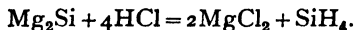
zinc, or with aluminium in an iron crucible, and dissolving out the metal from the cooled mass with acid :



Zinc gives long needle-shaped crystals, aluminium six-sided plates of graphitoidal silicon ; both varieties are made up of regular octahedra.

Silicon prepared in the electric furnace is a hard grey crystalline mass with a very high melting point and the appearance and electrical conductivity of graphite. It is used in the preparation of alloys (silicon bronze and manganese silicon bronze, etc.) on which it confers hardness and tensile strength. Crystalline silicon reacts with halogens, alkalis, etc., like amorphous silicon, but does not burn in oxygen even when strongly heated.

Silicon hydrides.—Silicon and hydrogen combine only at the temperature of the electric arc, forming a trace of silicon hydride : $\text{Si} + 2\text{H}_2 \rightleftharpoons \text{SiH}_4$. If magnesium powder and *dry* amorphous silica in the proportions of 2 : 1 by weight are heated in a crucible, magnesium silicide, which probably consists mainly of Mg_2Si , is formed as a bluish mass. This when acted upon with dilute hydrochloric acid in a flask from which air has been displaced by hydrogen, evolves a spontaneously inflammable gaseous mixture of silicon hydrides with hydrogen (Buff and Wöhler, 1857) :



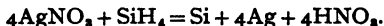
If the gas is bubbled through water, each bubble ignites in contact with the air and burns with a luminous flame producing a vortex ring of finely-divided silica : $\text{SiH}_4 + 2\text{O}_2 = \text{SiO}_2 + 2\text{H}_2\text{O}$ (*cf.* phosphine).

If the gas, after washing with water and drying with calcium chloride and phosphorus pentoxide, is passed through a tube cooled in liquid air, a liquid mixture of hydrides of silicon is condensed from which by fractionation several compounds may be isolated :

1. **Monosilane** SiH_4 is a colourless gas stable at the ordinary temperature, spontaneously inflammable if mixed with other hydrides and sometimes if pure ; it decomposes when passed through a red-hot tube, yielding twice its volume of hydrogen : $\text{SiH}_4 = \text{Si} + 2\text{H}_2$. By the action of caustic alkalis four times the volume of hydrogen is produced :



The gas precipitates copper silicide Cu_3Si from copper salts, and silver from silver salts :

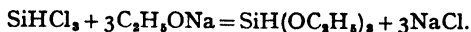


Pure monosilane is obtained by heating triethyl silicoformate with sodium :



The triethyl silicoformate (the silicon analogue of orthoformic ester,

$\text{CH}(\text{OC}_2\text{H}_5)_3$) is obtained by the action of silicon chloroform on absolute alcohol or sodium ethoxide NaOC_2H_5 :



2. **Disilane** Si_2H_6 , is a colourless gas, stable at the ordinary temperature but rapidly decomposed at 300° ; it inflames in the air, is soluble in benzene and carbon disulphide, and is decomposed by alkalis:



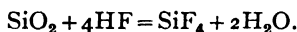
3. **Liquid hydrides** $\text{Si}_3\text{H}_8, \text{Si}_4\text{H}_{10}$ and **solid hydrides** of indefinite composition are also known.

Halogen compounds of silicon.—Compounds of silicon with all the halogens of the types SiX_4 , Si_2X_6 and SiHX_3 are known; isolated compounds of the types SiH_2X_2 and SiH_3X have been prepared and several halides not corresponding with the above types are known.

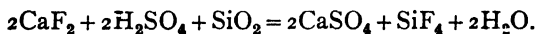
Silicon fluoride.—The amorphous and crystalline varieties of silicon ignite spontaneously in fluorine forming gaseous silicon fluoride SiF_4 . Pure silicon fluoride is obtained by heating barium fluosilicate in a copper tube :



The gas is more conveniently prepared by the action of hydrofluoric acid on silica (Scheele, 1771) :



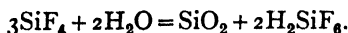
Since it is decomposed by water, some dehydrating agent is added. Usually a mixture of powdered fluorspar and white sand is heated in a thick glass flask with concentrated sulphuric acid :



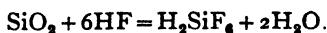
The gas is collected over mercury. To free it from hydrogen fluoride it may be passed over sodium fluoride. Silicates such as glass are also decomposed by hydrofluoric acid with evolution of silicon fluoride.

Silicon fluoride is a colourless incombustible strongly fuming gas, 3.6 times as dense as air. It solidifies without previous liquefaction at -97° under atmospheric pressure. The solid melts when warmed under pressure.

Hydrofluosilicic acid.—The reaction between silicon fluoride and water was discovered by Scheele in 1771 but first completely explained by Berzelius in 1823. It leads to the formation of gelatinous silica and soluble hydrofluosilicic acid :



If the gelatinous liquid so formed is mixed with hydrofluoric acid until the silica is just dissolved, more hydrofluosilicic acid is formed and the difficult filtration is avoided :



The acid is prepared on the large scale (for lead refining) by percolating aqueous hydrofluoric acid through sand, and as a by-product in the manufacture of superphosphate by treating minerals containing *apatite* with sulphuric acid (p. 342).

In the laboratory preparation, a mixture of 50 gm. of powdered fluorspar, 50 gm. of fine white sand and 200 c.c. of concentrated sulphuric acid is heated on a sand-bath in a stout glass flask with a safety-funnel containing mercury (thin glass is soon perforated and a stoneware bottle is sometimes used). The silicon fluoride (fuming in air) is passed into a cylinder,

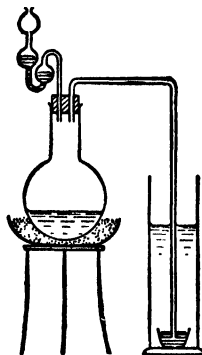
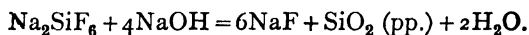
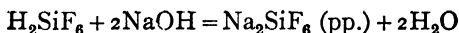


FIG. 189.—Preparation of hydrofluosilicic acid.

the dry delivery tube dipping under half an inch of mercury in a small crucible, over which water is afterwards poured. This is to prevent the tube becoming choked by the gelatinous silica (Fig. 189). The silica is deposited in small sacs each enclosing a bubble of gas; these should be broken down occasionally by stirring with a glass rod. The liquid is then filtered through linen and the silica when washed, dried and heated is very pure.

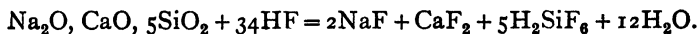
A concentrated solution of hydrofluosilicic acid fumes in the air. The anhydrous acid is not known and silicon fluoride and dry hydrogen fluoride do not react.

When solutions of hydrofluosilicic acid are titrated with alkali the following reactions occur:



The end-point with phenolphthalein is therefore reached when *six* molecules of base have been added per molecule of acid.

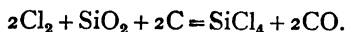
In etching glass with hydrofluoric acid solution (p. 176) the alkali metal (sodium or potassium) and calcium oxides are converted into fluorides, and the silica is converted into hydrofluosilicic acid. The approximate composition of common glass (p. 339) is Na_2O , CaO , 5SiO_2 , and the reaction with hydrofluoric acid may be represented by the equation:



Pure hydrofluosilicic acid does not corrode glass but on evaporation it decomposes: $\text{H}_2\text{SiF}_6 \rightleftharpoons \text{SiF}_4 + 2\text{HF}$, and the hydrofluoric acid set free corrodes a flask or porcelain basin. With steam at high temperatures crystals of silica are formed.

Salts of hydrofluosilicic acid called **fluosilicates** (or *silicofluorides*) are prepared by the action of gaseous silicon fluoride on the solid fluorides (the acid is decomposed by excess of alkalis): $\text{SiF}_4 + 2\text{NaF} = \text{Na}_2\text{SiF}_6$. The following are sparingly soluble and are precipitated when hydrofluosilicic acid is added to solutions of salts of the metals: Na_2SiF_6 , K_2SiF_6 , BaSiF_6 , rare earth fluo-silicates. The salts K_2SiF_6 and Na_2SiF_6 are formed as nearly transparent gelatinous precipitates; BaSiF_6 forms a white crystalline precipitate; calcium and strontium salts are not precipitated. The lithium salt Li_2SiF_6 is soluble in water.

Silicon chlorides.—[Silicon tetrachloride (Berzelius, 1823) is produced when amorphous silicon, or the mixture of this with magnesia obtained by heating silica with magnesium powder, is heated in a current of dry chlorine: $\text{Si} + 2\text{Cl}_2 = \text{SiCl}_4$.] Dry chlorine may also be passed over heated silicon-iron, or over an intimate mixture of precipitated silica and carbon strongly heated in a porcelain tube:



The products of reaction are cooled in a worm-tube, when silicon tetrachloride condenses as a colourless volatile liquid which fumes strongly in moist air owing to hydrolysis: $\text{SiCl}_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 4\text{HCl}$. It forms dense fumes with ammonia.

By passing silicon tetrachloride vapour over heated silicon, **silicon trichloride** Si_2Cl_6 (a liquid) is formed. Other chlorides are known.

Silicon chloroform (Buff and Wöhler, 1857) is prepared by passing hydrogen chloride over silicon (or the mixture of silicon and magnesia) at a dull red heat: $\text{Si} + 3\text{HCl} = \text{SiHCl}_3 + \text{H}_2$. The liquid condensed in a freezing mixture is fractionated to separate the less volatile silicon tetrachloride also produced. Silicon chloroform is a colourless very volatile fuming liquid, which is very inflammable and burns with a green-edged flame emitting white fumes of silica. A mixture of the vapour with air or oxygen explodes when brought in contact with a flame. At a red heat the vapour decomposes into Si, H_2 , HCl , SiCl_4 , and a trace of less volatile liquid.

By the action of ice-cold water on silicon chloroform **silicoformic anhydride** $(\text{HSiO})_2\text{O}$ is formed as a white solid, probably polymerised. This is a powerful reducing agent: $\text{H}_2\text{Si}_2\text{O}_3 + \text{O}_2 = 2\text{SiO}_2 + \text{H}_2\text{O}$ (cf. formic acid $\text{H}\cdot\text{CO}_2\text{H} + \text{O} = \text{CO}_2 + \text{H}_2\text{O}$). It is readily decomposed by dilute alkalis, with evolution of hydrogen: $\text{H}_2\text{Si}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{SiO}_2 + 2\text{H}_2$.

Silicon bromides SiBr_4 , Si_2Br_6 and iodides SiI_4 , Si_2I_6 , silicon bromoform SiHBr_3 and silicon iodoform SiHI_3 , are known.

Silica.—Silicon dioxide or *silica* occurs in nature both crystalline and amorphous. There are three main crystalline forms : *quartz*, *tridymite* and *cristobalite*, of which only quartz is common in nature.

Quartz (sp. gr. 2.648) or *rock-crystal* occurs sometimes in clear colourless apparently hexagonal crystals, used for optical apparatus, but more often in opaque ("milky") or coloured masses ("smoky-quartz", "cairn gorm"). Coloured varieties of quartz (*e.g.* purple, in *amethysts*) are used as gems. Sand consists of quartz grains which remain after the disintegration or "weathering" of rocks and have been crushed by movement in water.

The purest sand is white ("Calais sand"); yellow sand is coloured by ferric oxide, much of which may be dissolved by boiling with hydrochloric acid. "Singing sand", which emits a peculiar squeaking note when pressed, consists of rounded grains of nearly uniform size. It occurs in patches along with ordinary sand in various localities.

Tridymite (sp. gr. 2.26) occurs more rarely than quartz in minute crystals, usually six-sided plates, in cavities in some rocks.

Cristobalite (sp. gr. 2.32) is a tetragonal crystalline variety obtained by heating powdered amorphous (fused) silica at 1500°. It is very similar to tridymite. It is the stable form at high temperatures and is found in some volcanic rocks and in meteorites.

Quartz is the stable form below 870°, when it changes to tridymite, and tridymite changes into cristobalite at 1470°.

All varieties of silica fuse in the oxyhydrogen blowpipe and boil in the electric furnace. They become plastic before fusion and may be worked and blown like glass, or drawn into very fine thread. The amorphous vitreous *silica glass* has a very small coefficient of expansion and may be heated to redness and quenched in cold water without fracture. Quartz *crystals* easily crack when heated. Silica glass is transparent to the ultra-violet rays whilst ordinary glass is opaque. On heating silica glass at about 1100° it crystallises and becomes opaque. Hydrogen diffuses easily through heated silica glass, and helium even at room temperature.

The translucent *Vitreosil* is manufactured by fritting sand with an electrically-heated carbon rod or plate, evolution of gas from which prevents the fused silica from sticking to the carbon heater.

Pure amorphous silica is obtained as a white powder by decomposing silicon tetrachloride or tetrafluoride with water and heating the resulting gel. It is an impalpable white powder insoluble in water and all acids except phosphoric and hydrofluoric, but dissolves in hot concentrated caustic alkalis. Amorphous silica may be obtained by adding hydro-

chloric acid to a solution of an alkali silicate, when *gelatinous silica*, a hydrated form, is precipitated. The whole is evaporated to dryness on a water-bath, when the silica becomes insoluble in water. It is washed with boiling water till free from acid and alkali-chloride, and heated to redness in a platinum dish. This process is used for the determination of silica in minerals, glass, etc., these being first fused with sodium carbonate to form sodium silicate.

At high temperatures silica, a non-volatile acidic oxide, displaces volatile acids from their salts: $\text{Na}_2\text{SO}_4 + \text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{SO}_3$. It is, however, relatively inert and is used for making *refractory bricks* (ganister, Dinas brick, etc.) for furnace-linings. For this purpose pure sand or crushed quartz-rock is mixed with a little lime and clay and old broken firebrick ("grog"), and the mass moistened, moulded, and burnt.

Gelatinous silica freshly precipitated by the addition of hydrochloric acid to a fairly concentrated solution of sodium silicate ("water glass") is appreciably soluble in water, alkalis, sodium carbonate and acids.

If a dilute solution of sodium silicate is poured slowly with stirring into an excess of dilute hydrochloric acid, no precipitation occurs, although the reaction $\text{Na}_2\text{SiO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{SiO}_2 + \text{H}_2\text{O}$ has taken place (as may be shown by the electrical conductivity). If the liquid is poured on a dialyser, the sodium and chloride ions diffuse out leaving a clear colloidal solution or hydrosol of *silicic acid*, discovered by Graham in 1861. The colloidal solution may be concentrated by boiling in a flask to a certain extent, and by further evaporation over sulphuric acid forms a clear tasteless liquid with a feebly acid reaction. It is readily coagulated to a bluish-white nearly transparent jelly, *silica gel*. The hydrosol is more stable if small amounts of hydrochloric acid or caustic soda are added, but is at once coagulated by sodium carbonate or phosphate.

The *silicates*, which occur as minerals, are derived from *silicic acids*:

Orthosilicic acid H_4SiO_4

Disilicic acid $\text{H}_2\text{Si}_2\text{O}_5$

Metasilicic acid H_2SiO_3

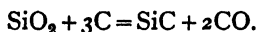
Trisilicic acid $\text{H}_8\text{Si}_3\text{O}_9$

and higher members. By loss of water from 1, 2, 3, etc., molecules of orthosilicic acid, the formulae of the other acids are obtained. Esters of some of these acids are known, *e.g.* ethyl orthosilicate $(\text{C}_2\text{H}_5)_4\text{SiO}_4$ and ethyl metasilicate $(\text{C}_2\text{H}_5)_2\text{SiO}_3$, and products corresponding with the formulae H_4SiO_4 and H_2SiO_3 are formed by their hydrolysis. The structures of mineral silicates have been determined by the X-ray method.*

Silicon monoxide SiO is a brown solid formed as a sublimate on heating a powdered mixture of silicon and silica in a vacuum at 1250°

* See *Text-Book of Inorganic Chemistry*, Chap. XXXIV.

Silicon carbide.—When a mixture of sand and crushed coke with a little salt and sawdust is strongly heated electrically by a carbon rod passing through the mass (*cf.* graphite), silicon carbide SiC is formed :



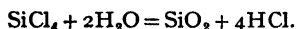
This compound, discovered by Acheson in 1891, is manufactured in large quantities at Niagara for use as an abrasive instead of emery since it is nearly as hard as diamond. The technical product (*e.g.* *Carborundum*) is a black coarsely-crystallised mass showing a play of iridescent colours. It has a very high melting point and may be used in furnace-linings ; it resists all reagents except fused sodium hydroxide exposed to air, which slowly acts upon it :

$$\text{SiC} + 4\text{NaOH} + 2\text{O}_2 = \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O}.$$

Pure silicon carbide forms transparent colourless or green six-sided plates, and is obtained by fusing silicon with carbon in the electric furnace,

Silicon also forms **nitrides**, *e.g.* Si_3N_4 , and a **sulphide** SiS_2 (by passing carbon disulphide vapour over heated silica and carbon).

The **atomic weight of silicon** is found by converting the chloride and bromide into oxide by decomposition with water :



(It should be noticed that a gravimetric precipitation as silver chloride cannot be used, as insoluble silica is precipitated ; the volumetric titration is possible and was used by Dumas.) The valency is found from the vapour density of SiCl_4 etc. ; the atomic heat is abnormal (p. 90). Marignac also used the isomorphism of silicofluorides and stannifluorides.

TIN

History.—It is supposed that some Egyptian hieroglyphics and the word *bedil* in the Old Testament refer to tin, and tin articles occur at least as early as the Eighteenth Dynasty (*c.* 1400 B.C.) in Egypt. The metal is mentioned by Homer as *kassiteros*, and Pliny speaks of *plumbum nigrum* (lead) and *plumbum candidum* (tin), observing that the latter was brought from the Islands of Cassiterides in the Atlantic. This refers to the British Isles, and the island Iktis on the coast of Britain which (according to Diodorus Siculus) was separated from the mainland only at high water, is St. Michael's Mount, Cornwall. The metal was afterwards called *stannum*.

Occurrence.—Tin occurs practically only as *tinstone* or *cassiterite*, the crystalline dioxide SnO_2 , which is found in Cornwall, the islands of Billiton, Banca and Singkep (Dutch East Indies), the Malay Peninsula and Burma, Nigeria and South Africa, and Bolivia. It occurs either massive in lodes or veins or as an alluvial deposit (*stream tin*). It is a dense mineral, easily separated from lighter rocks by washing the crushed ore. If *wolfram* (ferrous tungstate, FeWO_4) occurs with the tinstone

it cannot be separated in this way, since its density is the same as that of tinstone; it is removed by roasting and electromagnetic separation, or by heating with soda-ash when soluble sodium tungstate is formed.

Metallurgy.—The ore after separation from gangue, wolfram, etc., may be smelted. "Tin concentrate" which contains iron pyrites, arsenical pyrites or copper sulphide is first roasted in an inclined revolving tube-furnace (Oxland and Hocking's calciner, Fig. 222). Sulphur and arsenic are expelled as sulphur dioxide and arsenic trioxide (As_2O_3), the latter being condensed in chambers. Copper and iron form oxides and sulphates. The calcined ore discharged from the lower end of the furnace is cooled and soaked in water to remove copper sulphate which goes into solution (from which copper is recovered), and ferric oxide and light matter which are washed away. The treated ore, known as *black tin*, is mixed with ground anthracite coal and some lime or fluorspar to form a slag, and smelted in a reverberatory or a shaft furnace ("Cornish tin-castle"): $\text{SnO}_2 + 2\text{C} = \text{Sn} + 2\text{CO}$. The slags contain much tin and must be worked up by smelting in a blast furnace with coke.

The product is refined by *liquation*, i.e. by heating bars of the metal on the hearth of a reverberatory furnace, when the readily fusible tin flows away, leaving a dross consisting of an alloy of tin with copper, iron, and arsenic. The metal is finally fused and "poled" with billets of green wood, when the remaining impurities separate as a scum and pure metal is obtained. The scum and dross are worked up by smelting.

Properties.—Metallic tin has a bright white colour and a low melting point. When heated to 200° it becomes brittle and can be broken up by a hammer, yielding *grain-tin*. On slowly cooling molten tin crystals are formed. The metal is not very ductile and is too soft to be drawn, but is very malleable and can be rolled into *foil*, when the crystalline structure of the metal is destroyed. Since tin is not easily oxidised at the ordinary temperature, tinfoil is used for wrapping chocolate, etc., and tin tubes for containing tooth-paste. A rod of tin emits a peculiar creaking noise ("cry of tin") when bent, due to the friction of the crystalline particles. The lustre of tin is not impaired by exposure to air or water, either separately or conjointly, whereas lead is attacked. For this reason tin is used for *tinning* copper or iron vessels. These are first of all thoroughly cleaned and heated, and then molten tin is brushed over the surface, rosin and sal ammoniac being added as fluxes. Tin readily alloys with iron and copper. Tinplate is made by dipping clean sheets of iron (given a bright surface by "pickling" in dilute sulphuric acid) into molten tin covered with melted palm oil. The sheet then passes under a partition into molten tin covered with melted fat, and then through rollers to remove superfluous metal.

Tin is recovered from scrap tinplate by the *detinning process*. The material is washed with alkali to remove grease, rinsed and dried, and treated with chlorine gas in iron cylinders, kept cool. Volatile **stannic chloride** SnCl_4 is formed and the residue of iron scrap is hydraulically pressed into blocks and smelted in an open-hearth furnace.

When ordinary tin is strongly cooled it crumbles to a grey powder of smaller density. The transformation is quickest at -50° . **Grey tin** is an enantiotropic form (p. 24); the transition point is 13.2° . White tin is a metastable form at the ordinary temperature and in cold climates, *e.g.* in Russia, the massive metal sometimes falls to powder. (Aristotle seems to have known this.)

Tin oxidises when fused in air; the grey scum or dross forming on the surface is a mixture of tin dioxide and unchanged tin and on heating in air it is converted into **tin dioxide** SnO_2 , which is yellow when hot but becomes white on cooling. At a white heat tin burns in air with a white flame. Tin combines with chlorine and with sulphur.

Tin is only slowly attacked by dilute hydrochloric acid, but readily dissolves in hot concentrated hydrochloric acid forming a solution of **stannous chloride**: $\text{Sn} + 2\text{HCl} = \text{SnCl}_2 + \text{H}_2$. Dilute sulphuric acid does not dissolve pure tin; hot concentrated sulphuric acid gives **stannous sulphate** and sulphur dioxide, and some sulphur also separates, as with zinc: $\text{Sn} + 2\text{H}_2\text{SO}_4 = \text{SnSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$.

Dilute nitric acid slowly dissolves tin forming **stannous nitrate** and ammonium nitrate:



On strong cooling, the solution deposits crystals of $\text{Sn}(\text{NO}_3)_2 \cdot 20\text{H}_2\text{O}$. *Aqua regia* easily dissolves tin, forming stannic chloride; phosphoric acid dissolves tin to form **stannous phosphate** SnHPO_4 . Pure tin is scarcely attacked by boiling concentrated sodium hydroxide solution.

Concentrated nitric acid free from water has no action on tin, but in presence of a trace of water it acts violently, producing red fumes and forming a small quantity of soluble tin salt with an abundant white residue of hydrated stannic oxide, sometimes called **metastannic acid** $\text{H}_2\text{Sn}_5\text{O}_{11}$ (?). Boyle (1675) remarked that "*aqua fortis* eats up more tin than it dissolves."

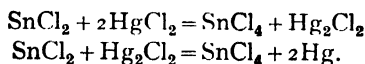
Tin forms important alloys, *e.g.* **bronze** (p. 308). A mixture of 1 part of lead and 2 parts of tin is ordinary *fine-solder* (*soft-solder* consists of equal parts of tin and lead, cheap solder is 7 lead and 3 tin). *Old pewter* contains 4 parts of tin and 1 part of lead, usually with a little antimony. *Britannia metal* and *modern pewter* consist of tin, antimony and copper.

Mirrors are sheets of very clean glass backed by pressing them on a surface of amalgamated tinfoil, but they are now mostly silvered. Tin forms with copper the definite compounds Cu_3Sn and Cu_5Sn , and with iron FeSn_2 . *Phosphor tin* is a white metallic coarsely crystalline mass formed by adding phosphorus to molten tin; the definite compound SnP is known. By adding phosphor tin to molten copper, *phosphor-bronze* is produced.

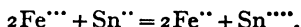
TIN COMPOUNDS

Tin forms two series of compounds; the **stannous** SnX_2 , in which tin is 2-valent, and the **stannic** SnX_4 , in which tin is 4-valent. The stannous compounds readily pass by oxidation into the stannic compounds. Stannous compounds are therefore reducing agents.

A solution of stannous chloride added to a solution of mercuric chloride gives first a white precipitate of calomel and if added in excess a grey precipitate of metallic mercury:

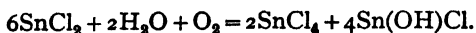


Stannous chloride added to a mixture of solutions of ferric chloride and potassium ferricyanide gives a precipitate of Prussian blue, owing to the reduction of the ferric salt to a ferrous salt:



Stannous oxide SnO is more basic than the dioxide SnO_2 , but both show feebly *acidic* properties forming **stannites** and **stannates** which are largely hydrolysed in solution. In solution, stannous salts ionise with formation of the stannous ion Sn^{++} , but stannic salts usually form complex ions, so that the existence of the stannic ion Sn^{++++} is doubtful.

Stannous compounds.—Tin (*e.g.* foil or granulated) readily dissolves in hot concentrated hydrochloric acid, a solution of **stannous chloride** being produced: $\text{Sn} + 2\text{HCl} = \text{SnCl}_2 + \text{H}_2$. On evaporating and cooling the solution deposits transparent readily fusible crystals of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. They lose acid on heating and the anhydrous salt is best prepared as a transparent glass by passing hydrogen chloride over heated tin. It is soluble in alcohol or ether, melts at 240° and boils at 603° , the vapour being associated: $\text{Sn}_2\text{Cl}_4 \rightleftharpoons 2\text{SnCl}_2$. The crystals of hydrated chloride, known as *tin salt*, do not give a clear solution except in a small amount of water or unless hydrochloric acid is added; with much water white **stannous oxychloride** $\text{Sn}(\text{OH})\text{Cl}$ is precipitated. Unless granulated tin is added the acid solution quickly becomes turbid from oxidation, stannous oxychloride being deposited and stannic chloride remaining in solution:



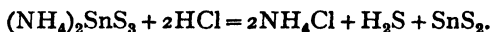
With concentrated hydrochloric acid, crystalline **hydrochlorostannous acid** $\text{HSnCl}_3 \cdot 3\text{H}_2\text{O}$, and in solution H_2SnCl_4 , are formed. These form stable crystalline salts, the **chlorostannites**, *e.g.* $(\text{NH}_4)_2\text{SnCl}_4$.

If a piece of zinc is suspended in a solution of stannous chloride, a bright crystalline deposit of tin is formed ("tin tree"). Large crystals of tin are produced by adding zinc dust suspended in water to a solution of stannous chloride.

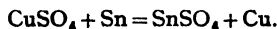
Sodium hydroxide added to a solution of stannous chloride gives a white precipitate of **hydrated stannous oxide**, $3\text{SnO} \cdot 2\text{H}_2\text{O}$. On heating this loses water and forms black **stannous oxide**, also formed by heating stannous oxalate: $\text{SnC}_2\text{O}_4 = \text{SnO} + \text{CO} + \text{CO}_2$. It smoulders when heated in air forming the dioxide SnO_2 . The hydrated oxide is soluble in acids forming stannous salts, and in alkali forming **stannites**, *e.g.* Na_2SnO_2 . The stannite solution has strong reducing properties, is unstable and deposits black SnO on standing. Very concentrated alkali decomposes hydrated stannous oxide into spongy tin and sodium stannate:



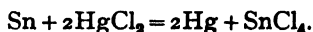
Stannous sulphide SnS is formed as a brown precipitate when hydrogen sulphide is passed into an acidified solution of stannous chloride, or as a grey crystalline mass on heating tin with sulphur. The brown precipitate (black when dry) is soluble in hot concentrated hydrochloric acid (arsenic trisulphide is insoluble); it is insoluble in alkali sulphides if these are free from excess of sulphur, but dissolves readily in the polysulphides, *e.g.* yellow ammonium sulphide, forming **thiostannates**: $\text{SnS} + (\text{NH}_4)_2\text{S}_2 = (\text{NH}_4)_2\text{SnS}_3$, from which acids precipitate **stannic** sulphide:



Stannous sulphate is formed by boiling tin with a solution of copper sulphate in dilute sulphuric acid, and crystallising:



Stannic compounds.—Tin combines at room temperature with chlorine gas to form a colourless volatile strongly fuming liquid **stannic chloride**, discovered by Libavius in 1605 and called *spiritus fumans Libavii*. He obtained it by distilling tin with corrosive sublimate:



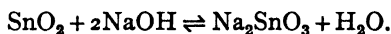
It is most conveniently prepared by passing chlorine to the bottom of a cooled vertical tube containing granulated tin until the metal is mostly converted to liquid stannic chloride, which is then distilled off. The vapour density corresponds with the formula SnCl_4 . With a small quantity of water it dissolves with evolution of heat, forming a clear

solution from which crystalline hydrates are obtained, *e.g.* $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. Stannic chloride is obtained in detinning scrap tinplate (p. 446). The hydrate is used as a mordant, especially for silk, and in "weighting" silk. By acting on $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ with hydrochloric acid gas and cooling at 0° , crystals of **hydrochlorostannic acid** $\text{H}_2\text{SnCl}_6 \cdot 6\text{H}_2\text{O}$ are formed. Stannic chloride combines with alkali chlorides to form the **chlorostannates**, *e.g.* $(\text{NH}_4)_2\text{SnCl}_6$, which crystallises anhydrous and was formerly used as a mordant in dyeing madder-reds and pinks (hence it was called "pink salt"); it has been superseded for this purpose by $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. Stannic chloride combines with many substances such as PCl_5 , POCl_3 , and NH_3 .

Stannic bromide SnBr_4 , a white fuming crystalline solid, and the **iodide** SnI_4 , red stable octahedral crystals, are formed directly. The **fluoride** SnF_4 , from SnCl_4 and anhydrous HF , forms white deliquescent crystals. It forms complex salts, *e.g.* K_2SnF_6 , analogous to silicofluorides.

Solutions of halogen compounds of 4-valent tin contain the un-ionised substances and hydrolysis products, *e.g.* colloidal stannic oxide, and the solution in hydrochloric acid contains the ion SnCl_6^{--} ; it is doubtful if the stannic ion Sn^{++++} is ever present as such.

Stannic oxide SnO_2 is known as *putty powder* and is used for polishing and in making opaque milk-glass and white glazes. It has acidic properties, forming **stannates** with alkalis:



They are hydrolysed by water and react alkaline.

Sodium stannate $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, used as a mordant, is prepared by fusing tin dioxide with caustic soda, extracting with hot water and crystallising. The ignited dioxide or the mineral tin-stone is insoluble in all acids except concentrated sulphuric, and does not dissolve in aqueous alkalis. It can be brought into solution only by fusion with caustic alkalis or alkali sulphides (forming thiostannates). Orthostannates are rare; the green cobalt salt Co_2SnO_4 is obtained by heating the oxides with a flux.

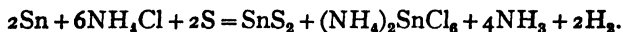
Colloidal stannic acid, formed in solutions of stannic chloride in water, readily gelatinises. The precipitate is soluble in excess of alkali hydroxide forming a stannate. Acids precipitate from this a gelatinous α -**stannic acid**, which on drying at 100° has the composition H_2SnO_3 , and is soluble in dilute acids or alkalis. The solution in dilute hydrochloric acid is identical with a solution of stannic chloride in water. On standing this solution slowly deposits β -**stannic acid**.

By the action of fairly concentrated nitric acid on tin stannous nitrate $\text{Sn}(\text{NO}_2)_2$ appears first to be formed but is rapidly oxidised by the nitric

acid to a white curdy powder of hydrated stannic oxide called β -stannic acid or metastannic acid, which differs from α -stannic acid in being insoluble in dilute acids. It is slightly soluble in water and the solution reddens litmus.

This variety of hydrated stannic oxide was given the formula $H_2Sn_2O_{11}$ ($5SnO_2 \cdot H_2O$) but the proportion of water is variable and the difference between the α - and β -acids seems to be due to something more than varying hydration. They have been regarded as colloids with particles of different sizes. Metastannic acid adsorbs phosphoric acid almost quantitatively from solutions and may be used in the separation of this acid in qualitative analysis, although it is not altogether satisfactory.

Stannic sulphide is formed by precipitating a solution of a stannic salt with hydrogen sulphide. The precipitate is light yellow but becomes black on drying; it is a mixture of the dioxide and disulphide. Crystalline SnS_2 is obtained as a residue of golden yellow glistening scales called *mosaic gold* by heating a mixture of tin amalgam or filings, sulphur and sal ammoniac, as described in a fourteenth-century Naples MS.; it is insoluble in acids but dissolves in *aqua regia* or alkalis:



Sodium orthothioannate $Na_4SnS_4 \cdot 18H_2O$ is formed by heating sodium stannate solution with sodium sulphide. From a solution of it boiled with precipitated SnS_2 , the metathioannate $Na_4SnS_4 \cdot 8H_2O$ crystallises at room temperature. The metathioannate is also formed by boiling tin and sulphur with a solution of sodium sulphide.

Traces of an unstable gaseous tin hydride SnH_4 are formed by the action of hydrochloric acid on an alloy of tin and magnesium.

It should be noticed that no definite oxysalts of 4-valent tin are known (the nitrate and sulphate are doubtful). Stannic tin resembles carbon and silicon in forming covalent compounds (p. 264); lead behaves similarly, although plumbic sulphate and acetate are known (p. 458). Bivalent tin and lead form oxysalts and in solution exist as ions Sn^{++} and Pb^{++} .

The atomic weight of tin is found from the analysis of $SnCl_4$ and $SnBr_4$; the valency is found from the vapour densities of $SnCl_4$ and tin triethyl $Sn_4(C_2H_5)_6$, and the atomic heat of tin.

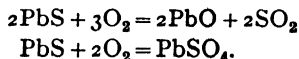
LEAD

History.—The metal lead is easily reduced from its ores and was known in ancient Babylonia and Egypt; it occurs in early bronzes and a small lead statue in the British Museum is attributed to the First Dynasty (3400 B.C.) in Egypt. The Greeks obtained lead from the Laurion mines but made little use of it. The Romans obtained lead from Spain, Gaul

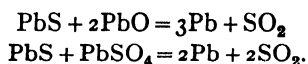
and Britain, and used it largely for cisterns, water pipes, etc. There is a considerable amount of Roman lead at Bath.

Occurrence.—Lead is widely distributed; traces occur in the native form but the chief ore is *galena*, the sulphide PbS , which is heavy, has a bright lustre and is found in many parts of the United Kingdom, Broken Hill (New South Wales), Spain and North America. Galena usually contains 0.01 to 0.1 per cent. of silver. The oxides *lead ochre* PbO and *plattnerite* PbO_2 are rare; the carbonate *cerussite* PbCO_3 , chlorophosphate *pyromorphite* $3\text{Pb}_3(\text{PO}_4)_2$, PbCl_2 , sulphate *anglesite* PbSO_4 , sulphocarbonate *leadhillite* $3\text{PbCO}_3 \cdot \text{PbSO}_4$, and basic sulphate *lanarkite* $\text{PbSO}_4 \cdot \text{PbO}$, all occur less abundantly than galena.

Metallurgy.—Lead is produced from galena by simple roasting in an oxidising atmosphere; its extraction was carried on in England during the Roman occupation. The process is mostly carried out in a reverberatory furnace (Fig. 147) known as a Flintshire furnace, or on the Scotch hearth (which has come into use again in a modified form), a flat hearth with *tuyeres* for the blast. The ore is first roasted at a moderate temperature when some galena is oxidised to oxide and sulphate:



The temperature is then raised, a little quicklime is added and the smelting reaction takes place, the remaining lead sulphide reacting with the two oxidised products:



The slag, which contains lead, is afterwards worked up by heating with lime and powdered coal in a small blast furnace.

Poorer ores and an increasing amount of richer ores are now smelted in small blast furnaces with coke. The ore is first roasted and the lead oxide is reduced in the blast furnace by the coke and carbon monoxide, the sulphide by the iron formed by reduction of the iron oxide in the charge (or added to the charge): $\text{PbS} + \text{Fe} = \text{FeS} + \text{Pb}$. Lead fume (chiefly PbO) formed during smelting is collected in flues and bag-filters, or by electrostatic precipitation.

Lead is also extracted by wet processes. The ore is roasted to sulphate, the soluble sulphates of manganese, magnesium, etc., dissolved out, and the lead sulphate dissolved in saturated brine containing chlorine. The solution is then electrolysed to deposit spongy lead.

The crude lead contains copper, antimony and bismuth, which render it hard. It is *softened* by melting on the hearth of a reverberatory furnace, until the foreign metals are oxidised and form a scum on the surface,

mixed with a little litharge (PbO). It is then desilvered (p. 319). In the *Harris process* the foreign metals are removed by treating the lead with molten caustic soda and sodium nitrate. Lead is refined by electrolysis in a solution of lead silicofluoride with a little gelatin, when a coherent deposit is formed. Commercial lead of 99.99 per cent. purity is easily obtained.

Properties.—Lead if perfectly pure has a silver-white lustre, but is usually bluish-grey. It is very soft, dense and fusible. It boils at a high temperature in a nearly perfect vacuum and the vapour is monatomic. Lead is plastic, especially when heated, when it may be “squirted” into wire by forcing it through a die under pressure, or “wiped” in forming pipe-joints in plumbing. Tubing is also formed by squirting. “Compo” tubing is of lead hardened with a little antimony. Bearing-metal alloys contain lead with calcium, barium, lithium, sodium, etc. Crystals of lead are obtained by precipitating it from a solution of the nitrate by a suspended piece of zinc (“lead tree”). Very beautiful crystals are obtained if the solution is gelatinised by adding gelatin.

Lead oxidises rapidly but superficially in moist air, a white film of hydroxide and carbonate being deposited. Pyrophoric lead (obtained by heating the tartrate in a tube and then sealing) ignites spontaneously in air. The metal is not attacked by pure water (except at the boiling point) or by dry air, but is rapidly corroded by soft water containing dissolved air, forming a loose deposit of hydroxide which is appreciably soluble in water, rendering the latter poisonous. The “plumbosolvency” is prevented by calcium bicarbonate or sulphate in hard water (p. 55). The addition of traces of tellurium reduces the corrosibility of lead and gives the metal greater strength.

Lead readily dissolves in dilute nitric acid or hot concentrated sulphuric acid forming salts of the bivalent Pb^{++} ion, which is colourless and resembles the barium ion Ba^{++} in many ways. It is a powerful cumulative poison, *i.e.* small quantities below the poisonous dose accumulate in the system and ultimately induce chronic poisoning. A characteristic symptom of lead poisoning, to which painters, plumbers and potters using lead and its compounds are liable, is a blue line on the edges of the gums.

Lead forms two series of compounds, the **plumbous compounds** (sometimes called “plumbic”)* in which it is 2-valent, and the **plumbic compounds** in which it is 4-valent.

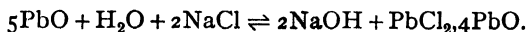
* The so-called “plumbous” compounds, *e.g.* Pb_2O said to be formed on heating lead oxalate, are mixtures of bivalent lead compounds and metallic lead: $2\text{PbC}_2\text{O}_4 = \text{Pb} + \text{PbO} + \text{CO} + 3\text{CO}_2$.

PLUMBOUS COMPOUNDS

Lead dichloride, plumbous chloride, or simply "lead chloride" PbCl_2 , occurs as the mineral *cotunnite* in some volcanic craters. *Mendipite* $\text{PbCl}_2 \cdot 2\text{PbO}$ and *matlockite* PbClF occur native. The chloride is slowly formed on heating the metal in chlorine. Boiling concentrated hydrochloric acid slowly dissolves lead: $\text{Pb} + 2\text{HCl} = \text{PbCl}_2 + \text{H}_2$. Lead chloride is usually prepared as a white precipitate by adding a chloride to a solution of a lead salt: $\text{Pb}^{++} + 2\text{Cl}' = \text{PbCl}_2$.

It is sparingly soluble in cold water but more soluble in boiling water and on cooling the hot solution anhydrous needles separate. Lead chloride melts readily and at a red heat boils, the vapour density corresponding with PbCl_2 . It dissolves in concentrated hydrochloric acid and crystalline salts, e.g. $\text{NH}_4\text{Pb}_2\text{Cl}_5$, are known.

On boiling litharge with a solution of common salt partial decomposition occurs with formation of sodium hydroxide (Scheele, 1773):



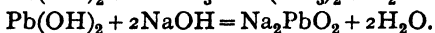
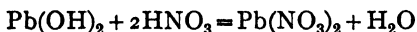
On heating the solid product yellow lead oxychloride $\text{PbCl}_2 \cdot 4\text{PbO}$ or *Turner's yellow* (1787), used as a pigment, is formed. Lead antimoniate is *Naples yellow*. *Cassel yellow* $\text{PbCl}_2 \cdot 7\text{PbO}$ is prepared by heating litharge with ammonium chloride.

Lead fluoride PbF_2 and lead bromide PbBr_2 are formed as white precipitates, and lead iodide PbI_2 as a yellow powder by adding potassium iodide solution to a solution of lead nitrate or acetate. On boiling it dissolves and on cooling golden-yellow spangles separate. It is soluble in a large excess of potassium iodide. Lead chlorate $\text{Pb}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, formed from litharge and chloric acid, evolves oxygen and chlorine on heating.

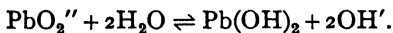
Lead monoxide is formed on heating lead in air. The grey dross so produced is a mixture of lead monoxide and metallic lead and if heated in an iron vessel it turns yellow, forming the monoxide PbO as a yellow powder (which darkens on heating) called *massicot*; if fused a reddish-yellow scaly crystalline mass of *litharge* is obtained. Lead monoxide is reduced by heating with carbon monoxide, hydrogen or carbon. Litharge obtained in the refining of silver is largely used in making flint-glass (see p. 340), preparing lead salts, and making paints and varnishes. It accelerates the absorption of oxygen by linseed oil, causing the latter to "dry" or form a solid oxidised compound. If litharge is boiled with water and olive-oil lead oleate, a sticky adhesive mass used in making lead-plaster, is formed and glycerin passes into solution. Two crystalline forms of PbO exist, a rhombic (yellow) obtained by heating lead in air,

and a tetragonal (red) formed by heating the hydroxide or carbonate.

Lead hydroxide $2\text{PbO}, \text{H}_2\text{O}$ or $\text{Pb}_2\text{O}(\text{OH})_2$ is formed as a white gelatinous precipitate on adding an alkali to a solution of a lead salt. It may be obtained crystalline. It loses water on heating forming the monoxide. The hydroxide is slightly soluble in water (as is PbO , which first forms the hydroxide) and the solution turns red litmus blue. It dissolves both in acids and bases forming lead salts and plumbites, respectively :



The **plumbite**, *e.g.* Na_2PbO_2 , is largely hydrolysed in solution :



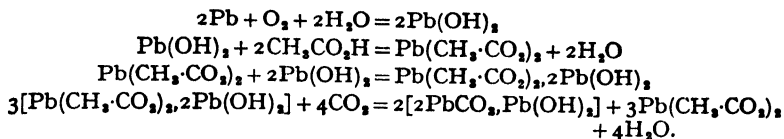
Ammonia does not dissolve lead hydroxide, since a sufficient concentration of hydroxide ions cannot be produced.

An important lead salt is the **acetate** $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2, 3\text{H}_2\text{O}$, known as *sugar of lead* on account of its sweet taste (*it is poisonous*). It is prepared by dissolving lead oxide (PbO) or carbonate in hot dilute acetic acid, evaporation and crystallisation. Excess of lead oxide forms a sparingly soluble basic salt. By boiling litharge with a solution of lead acetate a solution of a **basic acetate** called *Goulard's extract* is formed, which is used as a lotion.

Solutions of lead salts give a heavy white crystalline precipitate of **lead carbonate** PbCO_3 with a solution of alkali carbonate in the cold. The precipitate is sparingly soluble in water but dissolves readily in a solution of ammonium acetate. The **basic carbonate** $2\text{PbCO}_3, \text{Pb}(\text{OH})_2$ is the white pigment called *white lead*.

Good white lead is an *amorphous* powder ; it mixes readily with linseed oil and has a great covering power. If improperly made it is crystalline and has a considerable degree of transparency, its covering power being correspondingly reduced. White lead is readily blackened by hydrogen sulphide in the atmosphere. Its adulteration by the cheaper barium sulphate is detected by the insolubility of the latter in dilute nitric acid. *Venetian white* is a mixture of equal parts of white lead and barium sulphate ; in *Dutch white* the proportions are one to three.

The so-called *Dutch process* (really described by Theophrastos in 300 B.C.) produces the best quality of white lead. Rolls of sheet lead or grids of cast lead are placed in earthenware pots with vinegar. The pots are loosely covered and stacked in rows covered with planks and interstratified with spent tan-bark, the fermentation of which keeps the pots warm and produces carbon dioxide. Basic lead acetate is probably first produced and is then decomposed by the carbon dioxide, the lead acetate set free again entering into reaction :



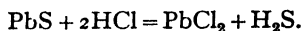
The plates after four or five weeks become incrustated with white lead. This is stripped off and ground and washed with water. The moist paste is dried in vacuum ovens. The presence of bismuth in the lead gives an objectionable colour to the product.

By boiling litharge with lead acetate solution a basic acetate is formed, which is precipitated by a stream of carbon dioxide. The white lead made by this method (*Thenard's process*) is of inferior quality. A better product is obtained by passing carbon dioxide into a suspension of lead oxide in water containing a little lead acetate.

Lead nitrate $\text{Pb}(\text{NO}_3)_2$ is deposited in anhydrous milky-white crystals, isomorphous with barium nitrate, from a solution of lead, litharge or lead carbonate in dilute nitric acid. Excess of lead oxide must not be used, as a basic salt is then formed.

Concentrated nitric acid precipitates lead nitrate from its solution, and lead is not dissolved by the concentrated acid because a protective coating of nitrate is formed. On heating, lead nitrate evolves nitrogen dioxide and oxygen (with decrepitation): $2\text{Pb}(\text{NO}_3)_2 = 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$. A **basic nitrate** $\text{Pb}(\text{OH})\text{NO}_3$ is formed in crystals by boiling a solution of the nitrate with litharge, and cooling.

Lead burns in sulphur vapour forming a greyish-black mass of **lead sulphide** PbS , which occurs as the mineral *galena*. The sulphide is also formed as a black precipitate on passing hydrogen sulphide into a solution of a lead salt. It dissolves in boiling *dilute* nitric acid with separation of sulphur; the concentrated acid converts it into the insoluble sulphate PbSO_4 . It dissolves in *hot* concentrated hydrochloric acid:

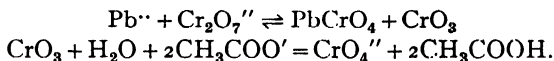


If hydrogen sulphide is passed into a solution of a lead salt containing excess of hydrochloric acid, a yellow or red precipitate is first formed consisting of $\text{PbS}, \text{PbCl}_2$. This afterwards forms black PbS (*cf.* HgS , p. 364).

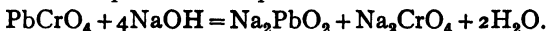
Lead sulphate PbSO_4 is formed by adding sulphuric acid or a sulphate to a solution of a lead salt. It is a heavy white powder, sparingly soluble in water and almost insoluble in dilute sulphuric acid. It dissolves in a warm solution of ammonium acetate since lead acetate is only slightly ionised (BaSO_4 is insoluble), or in hot concentrated sulphuric acid. With ammonia, a basic sulphate is formed. Lead sulphate occurs as the mineral *anglesite* in crystals usually isomorphous with barytes or celestine

but sometimes found as pseudomorphs of galena, and formed by oxidation of the latter.

Lead chromate PbCrO_4 is formed as a yellow precipitate insoluble in dilute but soluble in concentrated nitric acid (*cf.* BaCrO_4), and used as a pigment (*chrome yellow*). It is the least soluble lead salt and is precipitated by a chromate even in presence of ammonium acetate (*cf.* PbSO_4): $\text{Pb}^{++} + \text{CrO}_4^{--} = \text{PbCrO}_4$. The precipitation by a dichromate is incomplete unless sodium acetate is added:



PbCrO_4 dissolves to a yellow liquid in concentrated sodium hydroxide and a chromate and plumbite are produced:



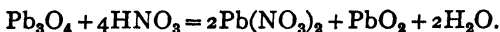
Lead cannot therefore be separated completely from acid radicals in the ordinary process used in qualitative analysis, boiling with sodium carbonate, if a chromate is present. If the solution is reduced with H_2S , a chromic salt and a precipitate of PbSO_4 are produced.

Orange or red basic lead chromates are formed when lead chromate is boiled with dilute caustic alkali and are used as pigments. Mixtures of lead chromate with lead sulphate or barium sulphate are also used as yellow pigments. In calico-printing the cloth is mordanted with a lead salt and then steeped in potassium chromate.

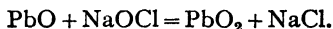
PLUMBIC COMPOUNDS

When white lead, massicot or finely-ground litharge is heated in air at about 340° it absorbs oxygen and forms a scarlet crystalline powder of *red lead* or *minium*: $6\text{PbO} + \text{O}_2 \rightleftharpoons 2\text{Pb}_3\text{O}_4$. Above 450° this decomposes again into lead monoxide and oxygen. Red lead is used to make cements with oil (it is not suitable for a pigment, as it oxidises the oil too rapidly) and in the manufacture of flint glass.

When red lead is stirred with concentrated nitric acid it is decomposed into lead monoxide which forms lead nitrate, and **lead dioxide** PbO_2 which remains as a chocolate-brown or puce-coloured powder on washing out the lead nitrate with hot water and drying. It may also be prepared by boiling red lead with diluted nitric acid, filtering and washing:



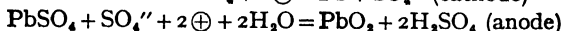
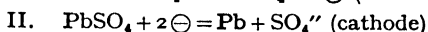
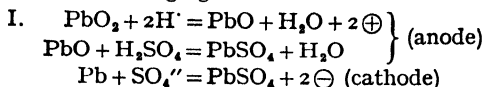
It is precipitated by bleaching powder or sodium hypochlorite solution from a solution of lead monoxide in sodium hydroxide, which contains a plumbite:



None of these preparations is pure lead dioxide, which is difficult to

obtain ; the best method is to electrolyse a dilute solution of lead nitrate when it is deposited on the anode.

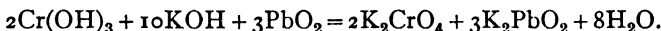
Lead dioxide is used as the anode in the lead accumulator, the cathode being of metallic lead and the electrolyte dilute sulphuric acid ; in the action of the cell both electrodes tend to be converted into lead sulphate, the reaction being reversed on charging the cell :



Lead dioxide is a powerful oxidising agent. A mixture with sulphur ignites on trituration, burning with a brilliant flame and forming lead sulphide. Lead dioxide becomes red hot when warmed in sulphur dioxide and lead sulphate is formed : $\text{PbO}_2 + \text{SO}_2 = \text{PbSO}_4$. If a manganous salt (*e.g.* MnSO_4) is boiled with nitric acid and lead dioxide a pink solution of permanganic acid is formed (*Crum's test*) :

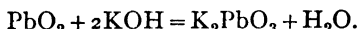


Chromic hydroxide in presence of alkali oxidises to a chromate :



Lead dioxide is a rather weak acidic oxide forming **plumbates**. When litharge and quicklime are heated together in air, the mass takes up oxygen forming calcium **orthoplumbate** : $4\text{CaO} + 2\text{PbO} + \text{O}_2 = 2\text{Ca}_2\text{PbO}_4$. On heating more strongly this decomposes evolving oxygen, and the method was formerly used in preparing oxygen from the atmosphere.

Potassium and sodium **metaplumbates** are formed when lead dioxide is added to potassium or sodium hydroxide fused in a silver dish :

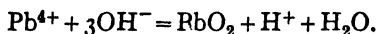


These salts are hydrolysed by water, PbO_2 being precipitated. Orthoplumbic acid H_4PbO_4 is not known, but **metaplumbic acid** H_2PbO_3 is deposited as a black powder on the anode by electrolysing a slightly alkaline solution of sodium lead tartrate. Minium, or red lead, may be regarded as lead orthoplumbate $\text{Pb}_2^{\text{II}}\text{PbO}_4^{\text{IV}}$.

Lead trioxide (or *sesquioxide*) Pb_2O_3 is a yellow powder precipitated by sodium hypochlorite from a cold solution of litharge in potassium hydroxide or by mixing solutions of potassium plumbite and plumbate. It is decomposed by dilute nitric acid into lead nitrate and lead dioxide and may be regarded as lead metaplumbate PbPbO_3 . It is said to be stable in air at $450^\circ\text{--}550^\circ$.

If lead dioxide is dissolved in *cold* concentrated hydrochloric acid and chlorine passed in a dark brown solution containing hydrochloroplumbic acid H_2PbCl_6 is formed. On addition of ammonium chloride this gives a yellow precipitate of ammonium chloroplumbate $(\text{NH}_4)_2\text{PbCl}_6$. When this is added to cold concentrated sulphuric acid the free acid H_2PbCl_6 breaks up at once and yellow liquid lead tetrachloride or plumbic chloride PbCl_4 is deposited. This readily decomposes (sometimes explosively) on warming with evolution of chlorine: $\text{PbCl}_4 = \text{PbCl}_2 + \text{Cl}_2$. Lead dioxide dissolves in *hot* concentrated hydrochloric acid with evolution of chlorine and formation of PbCl_2 .

On the addition of a *little* water, PbCl_4 forms a crystalline hydrate but it is readily hydrolysed to a brown precipitate of hydrated lead dioxide. The ion Pb^{4+} (like Sn^{4+}) is very unstable; the insoluble dioxide is usually formed when the ion might be expected:



Lead tetra-acetate $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ separates on cooling in colourless needles from a hot solution of red lead in glacial acetic acid (lead dioxide is insoluble). It is decomposed by water, lead dioxide being formed, but is the most stable plumbic salt.

A gaseous lead hydride has been described but its existence is very doubtful.

The atomic weight of lead has been found from the ratios $\text{PbCl}_2 : 2\text{AgCl}$ and $\text{PbBr}_2 : 2\text{AgBr}$. The valency is determined from the atomic heat and the vapour density of lead tetraethyl $\text{Pb}(\text{C}_2\text{H}_5)_4$. The atomic weight of lead is of special interest as it varies somewhat with the source from which the lead is derived when it has been formed from the radioactive decay of uranium ($\text{Pb} = 206$) or thorium ($\text{Pb} = 208$); ordinary lead has the atomic weight 207.2 and is a mixture of isotopes.

CHAPTER XXVIII

NITROGEN

GROUP V of the Periodic System comprises :

Sub-group a : vanadium, niobium, tantalum, protactinium.

Sub-group b : nitrogen, phosphorus, arsenic, antimony, bismuth.

Of these nitrogen and phosphorus are certainly non-metals and arsenic is usually regarded as a non-metal ; the rest are metals.

In typical compounds the elements are usually 3- or 5-valent, but occasionally 4-valent. The hydrides of sub-group *b* are all gaseous. Ammonia is a relatively strong base, phosphine (PH_3) is a very weak base, whilst arsine (AsH_3) and stibine (SbH_3) have no basic properties. Bismuth forms a very unstable gaseous hydride which dissolves in solutions of alkalis and may be feebly acidic. The oxides of nitrogen are more numerous than those of the other elements of sub-group *b*, of which only the types R_2O_3 , R_2O_5 , and sometimes R_2O_4 are known. The acidic character of the oxides, *i.e.* the electronegative character of the elements, diminishes from nitrogen to bismuth ; from arsenic onwards the oxides also show basic properties and stable salts are derived from Sb_2O_3 and Bi_2O_3 , *e.g.* $\text{Bi}(\text{NO}_3)_3$. The halogen compounds of phosphorus are completely hydrolysed by water: $\text{PCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCl}$; those of arsenic can exist in presence of excess of acid: $\text{AsCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_3 + 3\text{HCl}$; those of antimony and bismuth are only partly hydrolysed: $\text{BiCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{BiOCl} + 2\text{HCl}$.

NITROGEN

History.—In 1772 Daniel Rutherford allowed mice to breathe in air under a bell-jar and removed the fixed air (CO_2) by washing the residual gas with potash. A gas remained which did not support combustion or respiration but, unlike fixed air, was not absorbed by alkali or lime-water. Priestley (1772) burnt charcoal in a confined volume of air and absorbed the fixed air with alkali, also obtaining a " mephitic air " which he called *phlogisticated air*. Both considered that the gas was common air saturated with phlogiston emitted by the animal or combustible body. Scheele (1772) proved that air is a mixture of two gases, *fire air* which supports

combustion and respiration, and *foul air* which does not. Lavoisier (1775-6) furnished a decisive proof of this, and called Scheele's gas *azote* (Greek *a*, no; *zoe*, life), a name still used in France; the name nitrogen (Greek *nitron*, nitre) was suggested by Chaptal in 1790.

Atmospheric nitrogen was considered to be a pure substance until in 1894 Rayleigh and Ramsay found that it contains a little more than 1 per cent. by weight of an inert gas which, unlike nitrogen, does not combine with heated magnesium. The inert gas, the existence of which had been indicated by Cavendish in 1785, was called *argon* (Greek *argon*, sluggish); later experiments by Ramsay and Travers showed that it contains traces of other inactive gases: *helium*, *neon*, *krypton* and *xenon*.*

Occurrence.—Free nitrogen occurs in the atmosphere. The composition of air freed from moisture and carbon dioxide is roughly 4 volumes of nitrogen to 1 volume of oxygen; the exact figures (Leduc, 1896) are:

		By weight	By volume
Nitrogen	- - - -	75.5	78.06
Oxygen	- - - -	23.2	21.00
Argon, etc.	- - - -	1.3	0.94

The very nearly constant composition of dry atmospheric air was proved by Cavendish in 1783. Recent analyses (Benedict 1912; Carpenter 1937) indicate that the volume percentages of oxygen (20.939) and carbon dioxide (0.031) in uncontaminated air are very constant.

In air there are usually present, in addition to the above substances, minute quantities of carbon monoxide (in towns), hydrocarbons, hydrogen peroxide vapour, sulphur compounds such as hydrogen sulphide, sulphur dioxide and minute droplets of sulphuric acid, chlorides (especially near the sea), inorganic and organic dust, and moisture.

Traces of free nitrogen occur in volcanic gases and in gases evolved from coal; the gases evolved from some springs may contain over 95 per cent. by volume of nitrogen.

Nitrogen combined with hydrogen forms the base ammonia NH_3 , occurring in the free state and as salts in air, water, and volcanic products. In combination with oxygen nitrogen forms nitrous acid HNO_2 and nitric acid HNO_3 . Extensive deposits of sodium nitrate occur in Chile. Animal and vegetable organisms contain complex organic substances called proteins, with an average of 16 per cent. of nitrogen.

Preparation of nitrogen from air.—Nitrogen may be prepared: (a) from atmospheric air by removal of oxygen, (b) from nitrogen compounds. Atmospheric nitrogen is not quite pure since it contains about 1 per cent. of inactive gases, which give it a slightly higher density than pure nitrogen.

* Ramsay, *Gases of the Atmosphere*, 4th edit., 1915.

Oxygen is removed from air (previously freed from carbon dioxide) at the ordinary temperature by the action of phosphorus, moist iron filings, liver of sulphur, etc. Phosphorus, an alkaline solution of pyrogallol, an acid solution of chromous chloride, or a solution of cuprous chloride in hydrochloric acid or ammonia: $4\text{CuCl} + 4\text{HCl} + \text{O}_2 = 4\text{CuCl}_2 + 2\text{H}_2\text{O}$, remove atmospheric oxygen completely *on standing*. Metallic copper in contact with hydrochloric acid or ammonia also removes the oxygen.

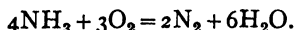
A long glass tube sealed at one end and fitted with a rubber stopper is divided into six equal volumes by labels. A solution of pyrogallol is poured in so as to occupy one division. A *small* piece of solid sodium hydroxide is slid into the upper part by means of crucible tongs, taking care that it does not fall into the liquid. The stopper is inserted and the tube shaken. The liquid becomes black owing to absorption of oxygen. The tube is opened under water; one of the remaining five divisions fills with water and four-fifths of the original volume of air remain as nitrogen.

Oxygen is removed from air by burning phosphorus but not quite completely.

A porcelain capsule containing a piece of phosphorus is floated on water and covered with a bell-jar divided from the water level into five equal volumes by strips of waxed paper (Fig. 190). The phosphorus is kindled by a hot wire and the stopper is inserted. When the phosphorus ceases to burn the fumes of phosphorus pentoxide P_2O_5 dissolve in the water. When the apparatus has cooled the water levels are equalised. The residual gas occupies four volumes and extinguishes a lighted taper.

Oxygen is removed by *slowly* passing air, dried and freed from carbon dioxide by solid caustic potash, over a long length of copper turnings heated to *bright* redness in a hard glass tube.

If air is bubbled through a warm concentrated solution of ammonia and the gas passed over a mixture of copper turnings and copper oxide heated to redness in a hard glass tube, the hydrogen of the ammonia is burnt by the oxygen of the air (Vernon Harcourt):



The gas so prepared is a mixture of atmospheric and pure nitrogen, and its density is intermediate between those of the two gases.

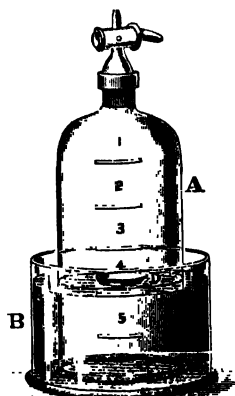


FIG. 190.—Burning phosphorus in air.

Nitrogen is made on the large scale either by passing air over red-hot copper, or mostly by the fractionation of liquid air (p. 119).

It should be noted that, as the boiling point of argon (-186°) is closer to that of oxygen (-183°) than to that of nitrogen (-196°), the nitrogen fraction contains very little argon; it contains a little oxygen, which is separated when necessary in the laboratory by passing the commercial nitrogen over copper turnings heated to bright redness.

The volumetric composition of air.—The oxygen in a measured volume of air may be removed by absorbents and the contraction measured. The most *accurate* method of finding the percentage by volume of oxygen in air is to explode a measured volume of air with excess of hydrogen. This may be done in a eudiometer over mercury. The hydrogen unites with the oxygen to form water which condenses to a liquid of negligible volume, hence the volume of oxygen is found by taking *one-third* of the measured contraction.

A convenient apparatus for gas analysis is the Hempel burette and absorption pipette shown in Fig. 191.

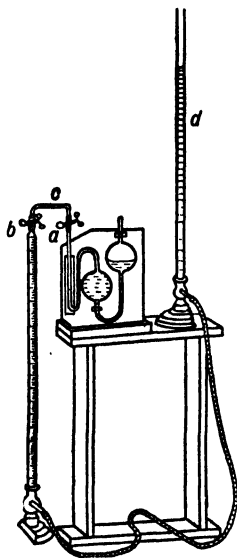


FIG. 191.—Hempel gas burette and pipette.

The burette and its levelling tube are mounted on two wooden stands weighted with lead and cut so that the two tubes may be brought close together. Connection with the pipette is made by glass capillary tube and rubber *pressure* tubing and the burette is closed with a spring clip.* The burette and capillary tube are filled with water and the sample of gas from the pipette is drawn into the burette and measured, water from the pipette being passed over to fill the capillary tube. The pipette is then filled with a suitable absorbent, re-connected with the burette and the gas passed into the pipette.

After shaking the gas is passed back into the burette and measured. If necessary the burette and pipette containing the gas sample may be filled with mercury.

Suitable absorbents are concentrated potassium hydroxide solution for carbon dioxide, alkaline pyrogallol for oxygen, ammoniacal cuprous chloride for carbon monoxide and acetylene, ferrous sulphate solution for nitric oxide, bromine water for ethylene.

* Burettes with glass taps are also obtainable but are more expensive

If gases are to be exploded (*e.g.* a mixture of hydrogen and air or a hydrocarbon gas and oxygen, see p. 403), an explosion pipette (Fig. 192) fitted with platinum sparking wires is used, the gas being confined over mercury. The gas and oxygen are measured separately in the burette and passed into the explosion pipette, in which the mixture is sparked, the tap being closed and the pressure tubing on the pipette being closed by a strong screw clip and a piece of glass rod.

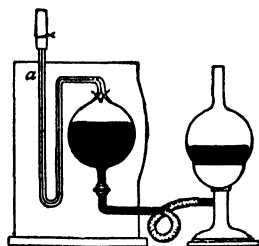


FIG. 192.—Explosion pipette.

The gravimetric composition of air.—The determination of the composition of air *by weight* is carried out by the method of Dumas and Boussingault (1841).

A long hard glass tube *a b* packed with bright copper turnings and fitted with a stopcock at each end is evacuated and weighed, put in the furnace, and heated to bright redness. It is connected at one end with a large weighed vacuous globe *V* closed by a stopcock and at the other with a bulb of potassium hydroxide solution *A* and two U-tubes, one *B* containing solid potassium hydroxide and the other *C* (next to the tube

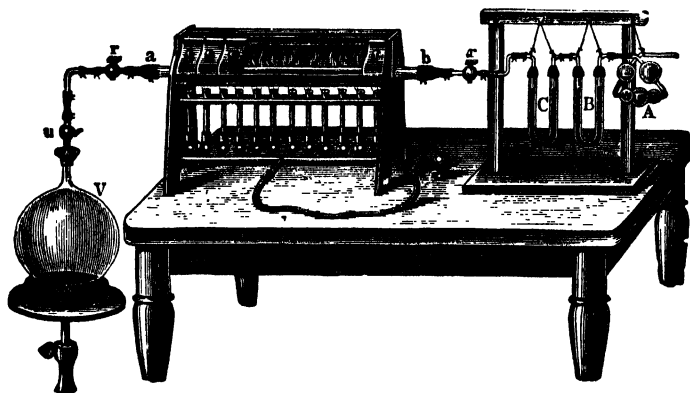


FIG. 193.—Gravimetric composition of air (Dumas and Boussingault's apparatus, modified).

containing the copper) calcium chloride, which remove carbon dioxide and moisture from the air (Fig. 193).

The stopcocks are slightly opened and air is allowed to pass *slowly* over the heated copper, the oxygen being absorbed to form copper oxide and the nitrogen passing on into the vacuous globe. When the globe is full of nitrogen the stopcocks are closed and the apparatus allowed to cool. The globe is weighed and thus the weight of the nitrogen found. The tube containing the copper and copper oxide is now weighed. The *nitrogen in this tube* is removed by a pump and the vacuous tube again weighed in order to find the weight of this nitrogen, which is added to that

in the globe. The increase in weight of the *vacuous* tube gives the weight of oxygen. The nitrogen as weighed contains the argon and other inert gases. These can be determined by a separate experiment (see p. 475).

Air is a mixture not a chemical compound.—That air is a mixture (really a *solution*) and not a compound of oxygen and nitrogen follows from the facts given below :

(i) Although the composition (when freed from water and carbon dioxide) is *nearly* constant it is not quite so, whereas every compound has a definite composition. The atomic ratio is also not simple but $N_{79}O_{21}$.

(ii) The constituents of air may be partly separated by diffusion (*atmoslysis*) through a porous pipe-clay tube into a vacuum, when the nitrogen passes through more rapidly than the oxygen.

(iii) The constituents of air may be separated by the fractional distillation of liquid air.

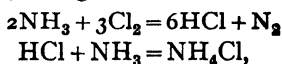
(iv) When air is shaken with water the dissolved part is richer in oxygen than the undissolved part.

(v) When oxygen and nitrogen are mixed there is no evolution or absorption of heat and all the properties of the mixture are intermediate between those of the constituents.

(vi) The relative density of air 14.4 corresponds with that of a mixture of *approximately* $4N_2 + O_2$; that of a compound N_4O would be 36.

Preparation of nitrogen from compounds.—Nitrogen is prepared in the laboratory by a number of methods which depend on the oxidation of ammonia, the hydrogen being removed and the nitrogen set free.

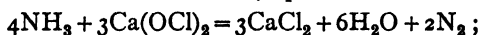
1. When chlorine gas is passed into, or bromine is added to, concentrated ammonia solution, nitrogen is evolved :



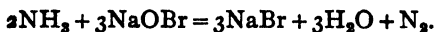
the reactions with bromine being similar.

In the case of chlorine the reaction is vigorous, flashes of light being seen in a darkened room ; care should be taken to keep the ammonia in excess otherwise the *very explosive* liquid nitrogen trichloride NCl_3 is formed (p. 474).

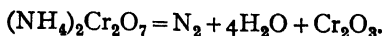
2. A thin paste of bleaching powder containing $Ca(OCl)_2$, calcium hypochlorite, may be run through a thistle funnel into concentrated ammonia solution warmed in a flask (explosions have been reported) :



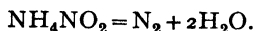
or sodium hypobromite solution (bromine freshly dissolved in cold sodium hydroxide solution) is dropped into concentrated ammonia solution :



3. When red crystals of ammonium dichromate are gently heated they decompose violently with flashes of light, nitrogen and steam are evolved and a voluminous green residue of chromic oxide is left :



4. The most convenient method of preparing nitrogen is to heat a solution containing ammonium nitrite, made by dissolving equimolecular amounts of sodium nitrite and ammonium chloride or sulphate in water :



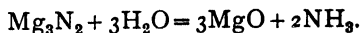
The gas evolved is washed with dilute sulphuric acid to remove ammonia, and collected over water.

The reaction may become violent and the liquid froth considerably. A little potassium dichromate may be added to the reaction mixture to prevent the formation of nitric oxide. Since the reaction is stopped by making the solution just alkaline with ammonia, it is probable that free nitrous acid is the active agent.

Nitrogen gas may be dried by calcium chloride, concentrated sulphuric acid or phosphorus pentoxide, and collected over mercury. Compressed nitrogen in cylinders may be bought ; it usually contains a little oxygen, which may be taken out by passing over copper turnings heated to *bright* redness.

Properties of nitrogen.—Nitrogen is a colourless odourless tasteless gas ; it does not support combustion or respiration although it is not poisonous ; it does not turn lime-water milky. It is sparingly soluble in water and has no action on litmus. It is liquefied by strong cooling. The liquid is colourless and on rapid evaporation under reduced pressure it forms a colourless ice-like solid.

Nitrogen is an inert element, since the heat of dissociation of the molecule is very large, but it combines directly with hydrogen and oxygen on sparking, with lithium slowly at room temperature to form the nitride Li_3N (more rapidly on heating), and with magnesium, calcium, strontium and barium at a red heat to form the nitrides M_3N_2 . It should be noted that sodium and potassium do not form nitrides in this way. Boron and aluminium form BN and AlN at a bright red heat ; silicon forms Si_3N_4 only at a white heat. Nitrides of many metals are formed by heating the finely divided metal or a salt in ammonia gas. Lithium nitride is decomposed by cold water, nitrides of alkaline earth elements by hot water, boron and aluminium nitrides on heating in steam. Ammonia and the oxide or hydroxide of the other element are formed :



The formation of magnesium nitride may be shown by heating with a blowpipe flame some magnesium powder in nitrogen in the short limb of a bent *hard* glass tube over mercury. The mercury slowly rises owing to absorption of nitrogen.

A peculiar form of nitrogen (**active nitrogen**) is formed by passing nitrogen at low pressure through a tube where it is subjected to an electric discharge; the gas after passing the discharge shows a yellow glow and is more active than ordinary nitrogen, combining with iodine, phosphorus, sulphur, mercury, etc. It probably owes its chemical activity to atomic nitrogen N.

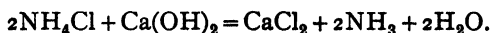
AMMONIA

History.—Ammonium chloride NH_4Cl called *sal ammoniac* or *sal ar-moni-ac*, appears to have been obtained in the Middle Ages from volcanoes in Central Asia, or prepared in Egypt from the soot formed on burning camels' dung. Gaseous ammonia was obtained by Priestley in 1774 by collecting over mercury; he called it *alkaline air* and found that when sparked it increased in volume and a combustible gas was formed: $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. Berthollet in 1785 showed that nitrogen and hydrogen were formed in this decomposition; the result was confirmed by Austin (1788), and the formula NH_3 established by Davy (1800) and Henry (1809).

Occurrence.—Traces of ammonia occur in the atmosphere: bottles containing hydrochloric acid become coated after a time with ammonium chloride. Ammonium chloride NH_4Cl , and sulphate $(\text{NH}_4)_2\text{SO}_4$, occur in volcanic districts; ammonia accompanies boric acid in the *soffioni* of Tuscany (p. 368). Small quantities of ammonium salts occur in plants and animals (*e.g.* in blood and in urine), in rock salt, in the soil, and in natural waters (as nitrite and nitrate).

Preparation.—Ammonia is formed from its elements when these are sparked together: $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ (Regnault, 1840). Deville (1864) pointed out that sparks will bring about both the formation **and** the decomposition of ammonia. The reaction is reversible and a state of equilibrium is set up in which 6 per cent. of NH_3 exists with 94 per cent. of the uncombined gases. If the mixture $\text{N}_2 + 3\text{H}_2$ and pure ammonia, respectively, are exposed in eudiometers to prolonged sparking contraction ensues in the first case and expansion in the second until the volumes and compositions are the same. A synthetic process is now employed on the large scale (p. 472).

In the laboratory ammonia gas is prepared by heating ammonium chloride with dry slaked lime:



A mixture of 50 gm. of powdered ammonium chloride with 150 gm. of powdered slaked lime ground in a mortar, is transferred to a 250 c.c. flask,

which is then filled with small lumps of quicklime. A cork and delivery tube leading to a drying tower filled with lumps of quicklime are fitted and the flask is heated on wire gauze. The gas is collected by upward displacement as it is lighter than air (Fig. 194). The jar is full when a piece of moist red litmus paper held near the mouth is turned strongly blue. Concentrated sulphuric acid reacts violently with the gas forming ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, and calcium chloride absorbs it forming a compound $\text{CaCl}_2 \cdot 8\text{NH}_3$, hence these reagents cannot be used to dry ammonia. Quicklime or pieces of potassium or sodium hydroxide may be used. Phosphorus pentoxide reacts with ammonia gas unless the gas is already very dry and pure.

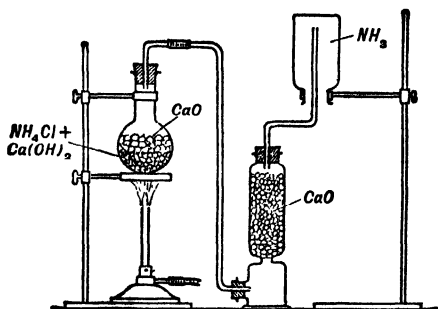
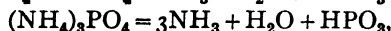
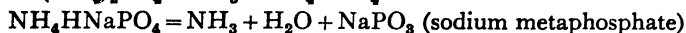
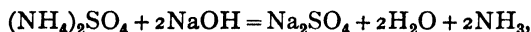


FIG. 194.—Preparation of ammonia gas.

Ammonia is evolved on heating ammonium sulphate, microcosmic salt or ammonium phosphate



but these are not convenient methods of preparation. It is also formed when ammonium salts are heated with sodium hydroxide solution :

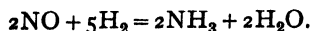


or when ammonium chloride is heated with litharge, when an oxychloride of lead $\text{PbCl}_2 \cdot 7\text{PbO}$ (p. 453) remains :



A convenient method of obtaining ammonia gas in small quantities is to warm the concentrated aqueous solution (*liquor ammoniae fortis*, sp. gr. 0.88) in a flask ; the gas is dried with quicklime. This is not of course strictly speaking a *preparation* of ammonia.

Ammonia is formed by the reduction of some oxygen compounds of nitrogen. A mixture of hydrogen and nitric oxide or a higher oxide of nitrogen (but not nitrous oxide), or even nitric acid vapour, passed over heated platinum, is reduced to ammonia :



Dilute nitric acid in presence of dilute sulphuric acid is reduced by zinc to ammonium sulphate : $\text{HNO}_3 + 8\text{H} = \text{NH}_3 + 3\text{H}_2\text{O}$. Sodium nitrate,

or more readily sodium nitrite, is reduced by zinc and hot sodium hydroxide solution, giving pure ammonia. Aluminium may be used instead of zinc, but nitrates are most easily reduced in alkaline solution by powdered Devarda's alloy, containing aluminium, copper and zinc. This method is used for the determination of nitrates or nitrites, the ammonia being distilled into standard acid.

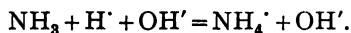
Ammonia is evolved on heating organic matter containing nitrogen (horn, bones, etc.) with *soda-lime* (prepared by slaking quicklime with sodium hydroxide solution and heating till dry), and ammonium sulphate is formed when the organic matter is heated for some time with concentrated sulphuric acid (*Kjeldahl's method* for the determination of nitrogen).

Ammonia is also formed from the nitrogen of coal as a by-product in the manufacture of coal gas (p. 405).

Properties.—Ammonia is a colourless gas lighter than air and fairly easily liquefied by cold or pressure, forming a colourless liquid freezing at a low temperature to an ice-like solid. The liquid may be obtained by cooling with a mixture of ice and crystalline calcium chloride; it is produced on a large scale by compressing the gas into steel coils cooled with water and is sent out in steel cylinders as *anhydrous ammonia*. The gas has a characteristic pungent smell, and is readily soluble in water.

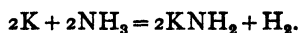
The solubility of ammonia gas may be demonstrated by the "fountain" experiment (Fig. 90), red litmus solution being used which is turned blue by the ammonia, which is alkaline.

The aqueous solution of ammonia is prepared by passing the gas into cold distilled water; the flask must be kept cool by running water over the outside since a considerable amount of heat is evolved. The liquid also expands considerably. The aqueous solution of ammonia is alkaline:

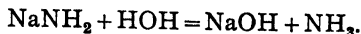


By strong cooling the crystalline hydrates $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $2\text{NH}_3 \cdot \text{H}_2\text{O}$ are obtained. A crystalline compound $\text{NH}_3 \cdot \text{H}_2\text{O}_2$ is formed by the action of ammonia on cold concentrated hydrogen peroxide. The solubility of ammonia in water obeys Henry's law above 100° and all the gas is expelled on boiling a solution.

If ammonia is passed over heated potassium or sodium, one-third of the hydrogen is replaced by the metal and *potassamide* KNH_2 or *sodamide* NaNH_2 is formed. These are white solids when pure and contain the univalent amino-group— NH_2 :

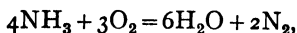


The alkali-metal amides are violently decomposed by water with evolution of ammonia :



Ammonia gas dried over quicklime and sodium hydroxide is passed over a piece of potassium heated in a hard glass bulb tube. The metal melts exposing a brilliant silvery surface and then boils emitting a green vapour and reaction begins. The hydrogen evolved may be kindled at the end of the tube and a brown mass of impure potassamide is left in the bulb.

Ammonia gas is not combustible in air and does not support combustion, but the flame of a taper before it is extinguished in the gas is surrounded by a large greenish-yellow flame due to decomposition of ammonia by heat and liberation of hydrogen : $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. Ammonia gas burns in oxygen with a greenish-yellow flame :



and a mixture of ammonia and oxygen explodes when kindled.

When a current of ammonia is passed through a tube surrounded by a wider tube through which oxygen gas is passing, and a burning taper is held over the tubes, the ammonia burns with a large three-coned yellowish flame (Fig. 195).

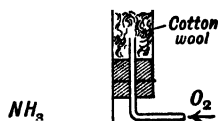


FIG. 195.—Combustion of ammonia in oxygen.

Oxygen is passed through a little concentrated ammonia warmed in a 200 c.c. conical flask and a red-hot spiral of platinum wire is suspended

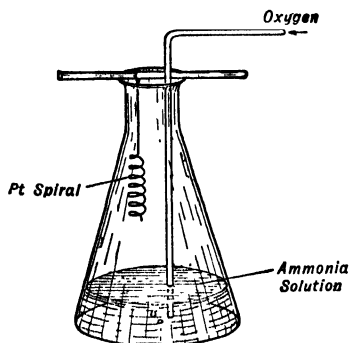
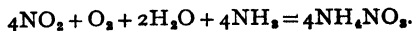
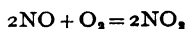
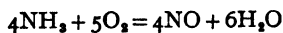


FIG. 196.—Catalytic combustion of ammonia.

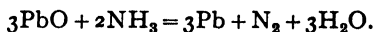
in the flask (Fig. 196). The mixture of ammonia and oxygen explodes feebly : * $4\text{NH}_3 + 3\text{O}_2 = 6\text{H}_2\text{O} + 2\text{N}_2$. The wire then cools, but after a short time it heats up again and there is another explosion when the gas mixture is renewed. During catalytic oxidation without explosion red oxides of nitrogen and white fumes of ammonium nitrate are formed :



* The explosion can be rather violent if a larger flask is used.

Ammonia gas may be detected (1) by its smell, (2) by the blueing of moist red litmus paper, (3) by the white fumes of ammonium chloride formed around a glass rod dipped in concentrated hydrochloric acid, (4) by blackening a piece of paper dipped in mercurous nitrate solution.

Ammonia gas reduces many heated oxides of metals (*e.g.* CuO, PbO; with copper oxide some nitric oxide is also formed, see p. 471).



Ammonia is readily absorbed by calcium to form $\text{Ca}(\text{NH}_2)_2$ and by dry silver chloride forming the compounds AgCl_3NH_3 and $2\text{AgCl}_3\text{NH}_3$. If the silver compound in one limb of a bent sealed tube is gently heated, liquid ammonia collects in the other limb immersed in a freezing mixture. On allowing the silver chloride to cool the ammonia is reabsorbed.

Ammonia is not easily decomposed by heat especially if diluted with an indifferent gas. It is decomposed by ultra-violet light and by radium emanation.

The composition of ammonia.—On *prolonged* sparking of ammonia gas in a eudiometer the volume is nearly doubled (a little ammonia remains undecomposed, see page 466). If oxygen is now added and a spark passed, or if the mixture is passed over palladium at 200° , water is formed and two-thirds of the contraction is equal to the volume of the hydrogen. (The composition of ammonia cannot be determined by exploding with oxygen since part of the nitrogen, up to 16 per cent., is also oxidised.)

Twenty c.c. of ammonia expanded to 40 c.c. on sparking. Oxygen was added till the volume was 157 c.c. After passing a spark the volume was 112 c.c. \therefore contraction on explosion with oxygen = 45 \therefore volume of hydrogen = $\frac{2}{3} \times 45 = 30$ \therefore volume of nitrogen = $40 - 30 = 10$. Thus 1 vol. of nitrogen + 3 vols. of hydrogen = 2 vols. of ammonia.

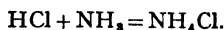
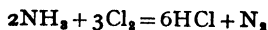
From Avogadro's hypothesis, it follows that 1 molecule of nitrogen and 3 molecules of hydrogen form 2 molecules of ammonia. Hence 1 molecule of ammonia contains $\frac{1}{2}$ a molecule (1 atom) of nitrogen* and $\frac{3}{2}$ molecules (3 atoms) of hydrogen and the formula is NH_3 . This may be *confirmed* by the density of the gas which shows that the molecular weight is 17.

The *volumetric composition* of ammonia may be also demonstrated by *Hofmann's experiment*.

A long tube (Fig. 197) is divided below the stopcock into three equal volumes by rubber bands and is filled with dry chlorine. The tube above

* This is actually a proof that the nitrogen molecule contains two atoms; the composition of nitric oxide (p. 488) is another. The ratio of specific heats of nitrogen, c_p/c_v , is 1.40, the value for a diatomic gas, and if the atomic weight of nitrogen is known the density of nitrogen gas leads to the formula N_2 .

the stopcock is one-third filled with concentrated ammonia solution, which is cautiously added in small portions to the chlorine, the tube being cooled by water. Each addition of ammonia reacts with a yellowish-green flame and the formation of white clouds of ammonium chloride :

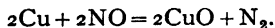
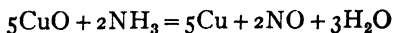
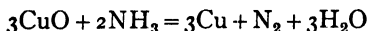


The fumes are washed down by shaking and dilute sulphuric acid is added to fix the excess of ammonia.

The tube is cooled by immersing in a large cylinder of water and the upper part above the tap is fitted with a cork and siphon tube dipping into water, the whole being filled with water. On opening the tap water runs into the long tube and it is found that the residual nitrogen occupies 1 vol.

The 3 vols. of chlorine have combined with 3 vols. of hydrogen from the ammonia to form HCl, \therefore 1 vol. of nitrogen is combined in ammonia with 3 vols. of hydrogen. Hence the formula is $(\text{NH}_3)_x$. In this case a density determination is necessary to show that $x = 1$.

In the *gravimetric analysis* of ammonia a measured volume of dry ammonia, the weight of which under the given conditions may be calculated from the density, is passed slowly through a hard glass tube containing red-hot copper oxide followed by copper heated to bright-redness to reduce oxides of nitrogen :



The water formed is collected in weighed calcium chloride tubes and the weight of hydrogen calculated. The nitrogen passing on is collected in a weighed exhausted globe (p. 463). In this way the weight ratio N : H is found to be 14 : 3. This is in the ratio of 1 atom of nitrogen to 3 atoms of hydrogen, hence the formula is $(\text{NH}_3)_x$. The volume of nitrogen collected occupies *half* the volume of the ammonia taken (pressure and temperature being the same), hence $x = 1$. The formula is *confirmed* by a density determination. (The apparatus of Fig. 193 may be adapted to this experiment.)

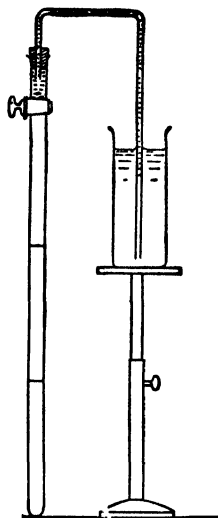
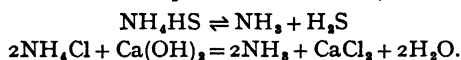


FIG. 197.—Volumetric composition of ammonia.

The manufacture of ammonia.—Ammonia (and ammonium salts) are made on the large scale by three processes.

1. From the *ammoniacal liquor* obtained as a by-product in the manufacture of coal gas or the carbonisation of coal in recovery coke-ovens (pp. 405, 409).

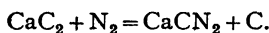
The liquor is heated in ammonia stills by steam to drive out the free ammonia or that produced by decomposition of the volatile salts (carbonate and sulphide), and the residue is then mixed with milk of lime and additional steam passed in to decompose the fixed salts (chloride and sulphate) :



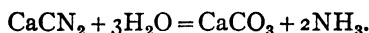
Most of the ammonia is now made directly from atmospheric nitrogen :

2. by the *cyanamide process*,
3. by direct *synthesis* from nitrogen and hydrogen. This is the most important method.

The cyanamide process.—In this process nitrogen gas is passed over calcium carbide heated at 1100° by carbon rods heated electrically inside drums of crushed carbide, or by raking the powdered carbide mixed with some calcium chloride or fluoride continuously through a furnace heated by electric arcs. Calcium cyanamide* mixed with graphite is formed as a dark grey mass called *nitrolim* or “cyanamide” :



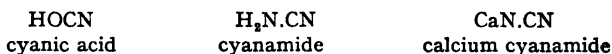
This is decomposed by heating with water under pressure :



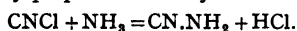
Synthetic ammonia.—It has been mentioned (p. 466) that small quantities of ammonia are formed by prolonged sparking of a mixture of nitrogen and hydrogen. Traces are also formed on passing the mixture through an ozoniser (p. 121). A very small quantity of ammonia is formed from nitrogen and hydrogen in presence of a heated catalyst at atmospheric pressure (0.4 per cent. by vol. at 400°). Increased pressure was first used by Nernst. Since a diminution of volume occurs in the exothermic reaction :



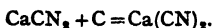
* Cyanamide is the amide of cyanic acid :



Cyanamide is most easily prepared from dry ammonia and cyanogen chloride :



Calcium cyanamide is converted into a crude cyanide by fusion with salt carbon and a little carbide :



Le Chatelier's principle (p. 230) shows that the amount of ammonia formed *in equilibrium* will increase with the pressure and diminish with rise of temperature.

In order to obtain appreciable amounts of ammonia the mixture of nitrogen and hydrogen, which must be very pure, is circulated by pumps under 100 to 200 atm. (*Haber process*) or even 900 to 1000 atm. pressure (*Claude process*) over a heated catalyst (500° to 550°) which may be iron with "promoters", e.g. molybdenum, or aluminium and potassium oxides. The ammonia formed in each circulation is removed by cooling and liquefaction or by absorption in water. The argon present in the atmospheric nitrogen, which accumulates, is blown off from time to time along with some of the mixture of nitrogen and hydrogen (Fig. 198). The percentages of ammonia by volume present *in equilibrium* under various conditions are given in the table below. When the plant is working at an economical rate, the gas does not remain in contact with the catalyst for long enough to allow of the attainment of equilibrium, so that the conversions are always smaller than these. The same considerations as to the effect of temperature on equilibrium and reaction velocity apply here as explained on p. 231 and also in the case of the manufacture of sulphur trioxide (p. 557).

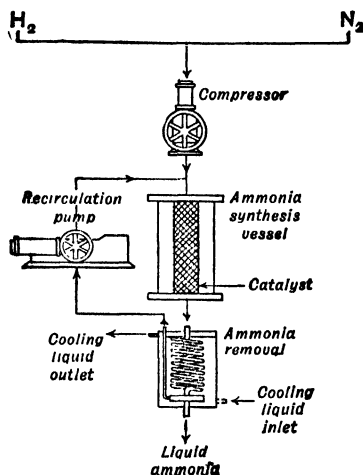


FIG. 198.—Synthetic ammonia apparatus (diagrammatic).

	10	100	300	1000 atm. pressure.
400° C.	3.85	25	47	80
500	1.2	10.6	26.4	57.5
550	0.76	6.8	19	41
600	0.5	4.5	14	31.5
700	0.23	2.2	7.3	13

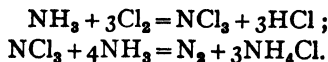
The hydrogen is prepared from water gas (p. 131), or by liquefying the more condensable gases in coke oven gas by cooling (p. 408), or electrolytically (p. 128). The nitrogen is obtained from air by liquefaction and fractionation. A mixture of $N_2 + 3H_2$ is also made directly from a mixture of producer gas (p. 420), water gas and steam by passing over a catalyst: $CO + H_2O \rightleftharpoons H_2 + CO_2$.

The catalyst vessels in the ammonia synthesis are of chrome steel (hydrogen permeates heated carbon steel) internally heated by electricity and the heat of reaction is used to heat the incoming gases. The ammonia may be liquefied for use in refrigeration plant, or dissolved in water, or

converted into ammonium sulphate by the calcium sulphate process (p. 304). Ammonium chloride is made from synthetic ammonia by the ammonia-soda process (p. 284).

The liquid (*anhydrous*) commercial synthetic ammonia is very pure but the synthetic ammonium salts are less pure, since sulphide is added to prevent corrosion of the iron evaporating pans.

Nitrogen trichloride.—Dulong (1811) by the action of chlorine on a solution of ammonium chloride obtained a yellow oily liquid which exploded violently and injured him severely. Davy in 1813, who was also injured by an explosion, showed that the liquid is a chloride of nitrogen. The formula NCl_3 was proved by Gattermann in 1888 by decomposing the oil by ammonia and precipitating the ammonium chloride formed with silver nitrate :



Nitrogen trichloride is prepared by inverting a flask of chlorine over a freshly prepared 25 per cent. solution of ammonium chloride, a lead

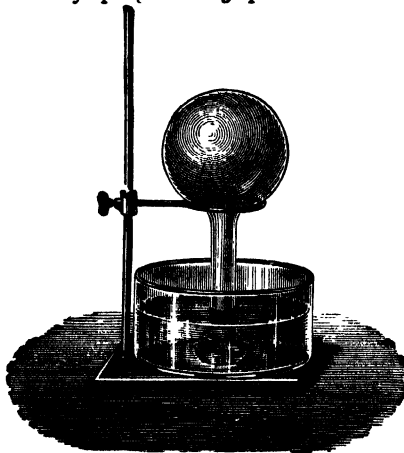


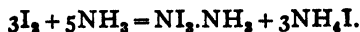
FIG. 199.—Preparation of nitrogen trichloride.

saucer being placed under the mouth of the flask (Fig. 199). The chlorine is absorbed and oily drops of the trichloride float on the surface of the solution. These fall into the lead saucer, which should be removed when a little liquid has collected in it.

Nitrogen trichloride detonates with great violence when heated or struck, or when exposed to sunlight, or on contact with phosphorus, many oils (including turpentine), fused caustic potash, phosphine, rubber, and nitric oxide. Cold water *slowly* decomposes it into nitrogen, chlorine, hydrochloric acid and nitrous acid.

It is a very dangerous substance and should on no account be prepared in a school laboratory or by any one except a very experienced chemist.

Nitrogen iodide.—By the action of iodine on a solution of ammonia Courtois in 1812 obtained a black explosive powder. This was examined by Gay-Lussac and by Davy in 1814, who showed that it contains nitrogen and iodine. The formula of "nitrogen iodide" was shown by Bunsen (1852) to be $\text{NI}_2 \cdot \text{NH}_3$:



To prepare nitrogen iodide, one gm. of iodine is gently triturated in a mortar with concentrated ammonia. A black powder is formed which is filtered off and is fairly stable when moist. The filter-paper is torn into a number of pieces, which are allowed to dry spontaneously. If one portion is touched with a feather tied to a stick it explodes. Violet fumes of iodine are evolved: $8\text{NI}_3 \cdot \text{NH}_3 = 5\text{N}_2 + 9\text{I}_2 + 6\text{NH}_4\text{I}$.

Nitrogen iodide is an active oxidising agent, oxidising sulphites to sulphates, arsenious acid to arsenic acid, etc.:

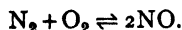


The true nitrogen tri-iodide NI_3 is a black powder formed by the action of gaseous ammonia on potassium iodobromide:



OXIDES AND OXY-ACIDS OF NITROGEN

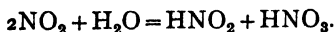
The union of nitrogen and oxygen.—Nitrogen and oxygen combine directly at high temperatures to form colourless nitric oxide gas:



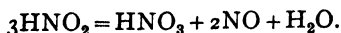
With excess of oxygen this forms on cooling red nitrogen dioxide gas:



Nitrogen dioxide dissolves in water forming a solution of nitrous acid and nitric acid:



Nitrous acid is unstable, and mostly decomposes into nitric acid and nitric oxide:



The nitric oxide is again oxidised if excess of oxygen is present, and finally all the oxides of nitrogen are converted into dilute nitric acid.

Electric sparks are passed through dry air in a globe (Fig. 200). After a time the air becomes yellowish in colour and if shaken with litmus solution the latter is turned red.

Cavendish (1785) passed sparks through a mixture of air and oxygen confined over mercury and potash solution in an inverted V-tube (Fig. 201). The oxides of nitrogen formed were absorbed by the alkali and the residual oxygen was then absorbed by a solution of liver of sulphur, only a very small bubble of gas remaining (probably argon; see p. 460).

Cavendish says: "We may safely conclude that in the present experiments the phlogisticated air [N] was enabled, by means of the electric

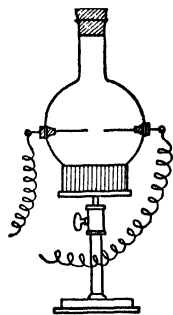


FIG. 200.—Combination of nitrogen and oxygen by sparking.

spark, to unite to, or form a chemical combination with, the dephlogisticated air [O], and was thereby reduced to nitrous [nitric] acid, which united with the soap-les [potash] and formed a solution of nitre; for in these experiments those two airs actually disappeared, and nitrous acid was actually formed in their room."

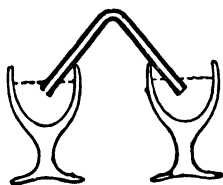


FIG. 201.—Cavendish's apparatus for sparking air over potash solution.

By a suitable modification of this experiment the amount of argon (and other inert gases, p. 460) in a sample of atmospheric nitrogen may be determined.

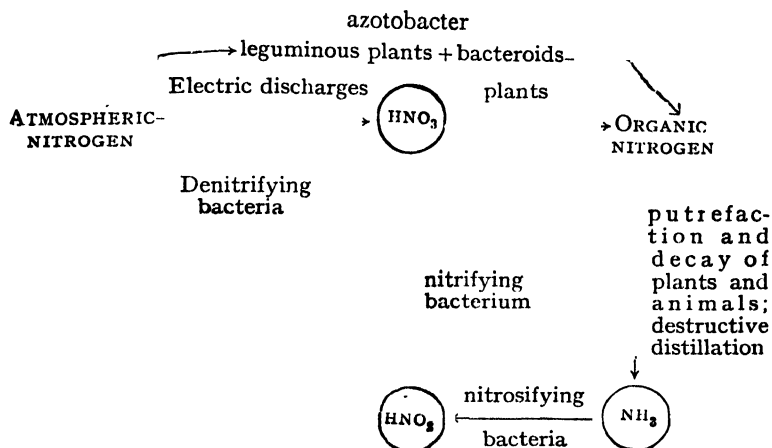
Nitric acid is also formed by burning hydrogen in oxygen containing some nitrogen, and when a mixture of detonating gas (2 vols. of H_2 + 1 vol. of O_2) with less than twice its volume of air is exploded by a spark. With more air the temperature of explosion is too low to form nitric acid. Thus no acid is formed on exploding a mixture of hydrogen and air. This reaction leads to errors in gas analysis when combustible gases mixed with nitrogen are exploded with oxygen.

The nitrogen cycle.—Nitric acid formed by electrical discharges in the atmosphere is washed down by rain. Besides the nitric acid so produced, which is absorbed from the soil in the form of nitrates by plants, leguminous plants can take up atmospheric nitrogen which is converted into organic nitrogen by the agency of micro-organisms which occur in nodules on the roots. The nitrogen-fixing bacterium is called *Pseudomonas radiculicola*; when it enters the plant by way of the root-hairs it develops into rods and when nodules are formed on the roots these rods associate into characteristic Y-shaped organisms called *bacteroids*. A bacterium *Azotobacter chroococcum* present in soil, capable of utilising elementary nitrogen in the presence of calcium carbonate, plays a large part in forming and maintaining the supply of combined nitrogen in the soil. The organic nitrogen compounds elaborated by plants serve as food for herbivorous animals, and the proteins of the latter are utilised in turn by carnivora.

When the bodies of animals and plants decay, or are subjected to destructive distillation, ammonia is produced. In the soil this is oxidised by *nitrosifying bacteria* to nitrites, and these by the *nitrifying bacterium* to nitrates, the latter again serving for the nourishment of plants. A portion of the nitrogen, however, is again set free by the action of *denitrifying bacteria* in the soil; the commonest is *B. denitrificans*. Both nitrosifying and nitrifying bacteria derive their carbon from carbon dioxide. The bacterium which produces nitrites is *B. nitrosomonas* in several varieties; that which converts nitrites into nitrates is *B. nitrobacter*. A few plants can assimilate nitrogen from ammonium compounds and some from nitrites.*

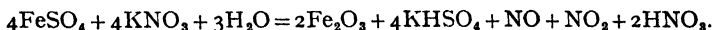
* See Brimble, *Intermediate Botany*, pp. 169 f.

The nitrogen cycle in nature may be represented diagrammatically as shown below.



NITRIC ACID

History.—Nitric acid appears to have been known in Europe about 1100 A.D. if not earlier. It was at first obtained by distilling saltpetre with green vitriol :



Glauber about 1658 obtained a more concentrated fuming acid by distilling nitre with concentrated sulphuric acid. The acid was therefore known as *spiritus nitri Glauberi*. The presence of oxygen in nitric acid was demonstrated by Lavoisier in 1776 by heating nitrate of mercury, which evolved oxygen. Scheele in 1777 showed that nitric acid vapour is decomposed by heat.

This may be demonstrated by pouring about 5 c.c. of concentrated nitric acid into the bowl of a clay tobacco pipe, the stem of which is strongly heated as shown in Fig. 202. The acid is decomposed on passing through the hot tube and bubbles of oxygen collect in the test-tube :



The NO_2 dissolves in the water.

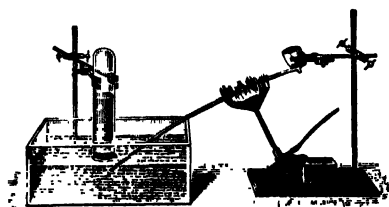
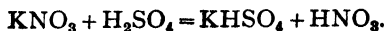
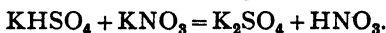


FIG. 202.—Decomposition of nitric acid by heat.

Preparation.—Nitric acid is prepared in the laboratory by distilling potassium or sodium nitrate with concentrated sulphuric acid in a retort ;



The acid distilling over is collected in a cooled receiver. If excess of nitre is used at a high temperature, further decomposition occurs, the acid sulphate being converted into normal sulphate :



A glass retort then usually cracks, and part of the acid is always decomposed with production of red gaseous oxides of nitrogen which dissolve in the acid, colouring it yellow :



On the large scale sodium nitrate is distilled in an iron retort with concentrated sulphuric acid in such proportions as will give equimolecular amounts of acid and normal sodium sulphates :



One or two tons of previously dried sodium nitrate (Chile nitre) are heated with rather more than this weight of concentrated sulphuric acid in a large cast-iron cylinder or pot built in a brickwork furnace so as to allow of very uniform heating (Fig. 203). Nitric acid *vapour* does not

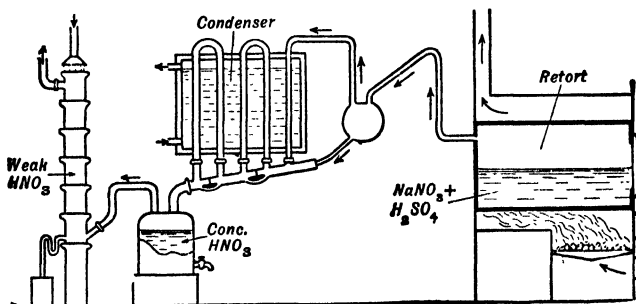


FIG. 203.—Manufacture of nitric acid.

attack iron, which is corroded by the liquid acid. At the top of the retort is a manhole for introducing the charge, and an outlet for the acid vapour. (The cylinder is charged from the end.)

The acid is condensed in some type of cooler, consisting of vitreous silica spirals cooled in water, stoneware U-tubes or horizontal glass tubes cooled by air and water, S-shaped tubes of silicon iron, or large stoneware Woulfe's bottles. The red oxides of nitrogen also produced are condensed by water in a stoneware tower at the end, packed with hollow stoneware cylinders or balls :



The liquid residue in the retort is run out from an outlet at the bottom and allowed to solidify ; it is a mixture or compound of about equimolecular proportions of NaHSO_4 and Na_2SO_4 , called *nitre cake*.

The yellow acid may be made colourless by warming to $60^\circ\text{--}80^\circ$ and bubbling dry air through it, when the nitrogen dioxide (NO_2) in solution is

gradually removed. Sometimes the distillation of the nitrate and sulphuric acid is carried out under reduced pressure, when less nitric acid is decomposed.

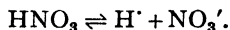
Properties.—Concentrated nitric acid when pure is a colourless liquid of density 1.52, which fumes strongly in moist air. It has a very corrosive action on the skin and cloth and stains them bright yellow.

Nitric acid vapour is decomposed by light. If a bottle half filled with acid is exposed to light the nitrogen dioxide formed dissolves in the liquid and renders it yellow. The liquid in a completely filled bottle remains colourless.

A yellow *fuming nitric acid* containing oxides of nitrogen and used as an oxidising agent is prepared by distilling nitre and sulphuric acid with a little starch, which reduces a portion of the nitric acid to N_2O_3 and NO_2 which dissolve in the acid (p. 492).

Pure nitric acid is unstable and can be obtained only by adding nitrogen pentoxide (N_2O_5) to very concentrated nitric acid. It begins to boil at 78° but is decomposed until a stable constant boiling point solution containing 68 per cent. of HNO_3 distils over at 120.5° at 760 mm. The concentration varies with the pressure (see p. 158). Heat is evolved and contraction occurs on mixing concentrated nitric acid with water; the maximum effect occurs with the ratio $3HNO_3 + H_2O$ but this is not a definite hydrate, the crystalline solid hydrates being $HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$.

Nitric acid is a strong acid, largely ionised in solution :



It is monobasic and forms salts, the nitrates, which are obtained by the action of nitric acid on the metals (when oxides of nitrogen, not hydrogen, are usually evolved), on the oxides or hydroxides, or on the carbonates. Some acid nitrates, *e.g.* NH_4NO_3 , HNO_3 and $NH_4NO_3 \cdot 2HNO_3$ are known.

Nitric acid also acts as an oxidising agent. Hot concentrated nitric acid oxidises iodine to iodic acid HIO_3 , phosphorus is oxidised to phosphorous and phosphoric acids (white phosphorus may cause an explosion), sulphur is oxidised to sulphuric acid, arsenious oxide to arsenic acid. Tin is oxidised by concentrated nitric acid in the cold with evolution of red fumes and a white residue of hydrated stannic oxide remains. Burning charcoal burns brilliantly in the concentrated acid, and sawdust is inflamed when heated on a sand-bath until it begins to char, and a few drops of fuming nitric acid are poured on it from a test-tube. (Care is necessary in this experiment.)

Oil of turpentine explodes with concentrated nitric acid with evolution of black clouds of carbon. Alcohol is violently oxidised with

the production of red fumes and a variety of substances, and sometimes with explosion.

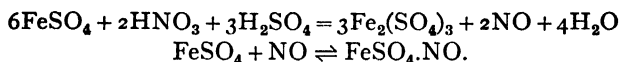
Hydrogen sulphide is not oxidised by pure nitric acid but in presence of nitrogen oxides it is decomposed with separation of sulphur (see p. 550). Stannous chloride in hydrochloric acid is oxidised to stannic chloride and the nitric acid is reduced to nitrous oxide and ammonia.

A mixture of concentrated hydrochloric and nitric acids when warmed evolves a gaseous mixture of chlorine and nitrosyl chloride NOCl :



Since chlorine is produced, the mixture of acids dissolves gold and platinum and is called *aqua regia*.

Ferrous salts reduce nitric acid to nitric oxide NO, and this dissolves in the excess of ferrous salt in solution to form in the cold a black solution, which evolves nitric oxide on heating :



The student should distinguish carefully between the reduction of nitric acid to nitric oxide, when the ferrous salt is oxidised to a ferric salt, and the solution of the nitric oxide in the ferrous salt to form the black compound $\text{FeSO}_4.\text{NO}$, which is decomposed by heat into nitric oxide and the ferrous salt.

This is used in the " ring test " for nitric acid and nitrates. In the case of nitrates, *concentrated* sulphuric acid must be added before the colour appears (*nitrites* give the reaction with *dilute* acid).

A few crystals of ferrous sulphate are dissolved in a cold dilute solution of a nitrate in a test-tube, and pure concentrated sulphuric acid is poured carefully into the liquid so as to form a heavy layer below. At the junction of the liquids a black ring (purple if only traces of nitrate are present) is formed (Fig. 204). On shaking, the black colour disappears, bubbles of nitric oxide are evolved, and a solution of ferric and ferrous sulphates remains.

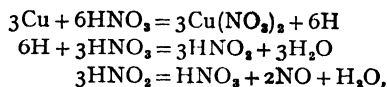


FIG. 204.—The ring test for nitrates.

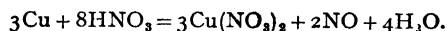
Other tests for nitric acid and nitrates are : (i) the red colour produced with a solution of brucine in concentrated sulphuric acid ; (ii) the deep-blue colour with a solution of diphenylamine in concentrated sulphuric acid ; (iii) the evolution of red oxides of nitrogen when the substance is heated with concentrated sulphuric acid and copper turnings ; (iv) *nitron* reagent (1 per cent. in 5 per cent. acetic acid) forms a white crystalline precipitate of nitron nitrate $\text{C}_{30}\text{H}_{18}\text{N}_4.\text{HNO}_3$, on adding 5 drops of reagent and 1 drop of dilute sulphuric acid to 5 c.c. of nitrate solution. Reactions (i) and (ii) are given by other oxidising agents, e.g. chlorates.

The action of nitric acid on metals.—Nearly all metals, except platinum, gold and pure aluminium, are attacked by dilute or concentrated nitric acid. Tin, antimony and arsenic are converted into oxides. The remaining metals form nitrates. Iron and chromium become “passive” in concentrated acid; lead is covered with a protective film of nitrate. During the reactions part of the acid is reduced with the formation of the oxides NO_2 , N_2O_3 , NO and N_2O , free nitrogen, hydroxylamine (NH_2OH) and ammonia. The products depend on the metal, the temperature, the concentration of the acid, and the presence of the products of reaction in the solution. Hydrogen is evolved by magnesium or manganese and cold dilute (1 or 2 per cent.) nitric acid: $\text{Mg} + 2\text{HNO}_3 = \text{Mg}(\text{NO}_3)_2 + \text{H}_2$.

Armstrong and Acworth (1877) supposed that nascent hydrogen reduces the nitric acid, *e.g.*



giving by addition the usual equation:

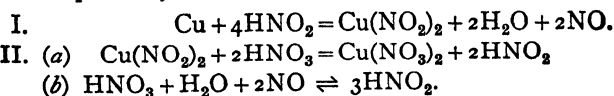


Divers says Ag, Cu, Bi and Hg give NO but no ammonia or hydroxylamine with nitric acid; Fe, Zn, Sn, Cd, Mn and Mg form ammonia and N_2O . Copper dissolves in hydrobromic acid (sp. gr. 1.5) and hydriodic acid (sp. gr. 1.7) on heating, with evolution of *hydrogen*.

Veley (1890) showed that *pure* nitric acid in the absence of nitrous acid scarcely acts on copper, silver, bismuth or mercury. Other metals react in the absence of nitrous acid but more slowly than when it is present. Since nitrous acid is formed in the reaction, the speed of the reaction increases as it proceeds.

Pieces of clean copper foil are immersed in three glasses containing: (a) 50 c.c. of 50 per cent. nitric acid; (b) 50 c.c. of this nitric acid + 5 c.c. of hydrogen peroxide (20 vols.); (c) 50 c.c. of nitric acid + 1 c.c. of hydrazine hydrate solution. The foil in (a) is at once violently attacked; those in (b) and (c) remain for a time without change. The hydrogen peroxide oxidises nitrous acid: $\text{HNO}_2 + \text{H}_2\text{O}_2 = \text{HNO}_3 + \text{H}_2\text{O}$, whilst hydrazine decomposes it: $\text{HNO}_2 + \text{N}_2\text{H}_4 = \text{HN}_3 + 2\text{H}_2\text{O}$.

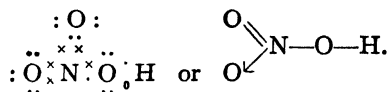
According to Veley, nitric oxide is a primary product formed from traces of nitrous acid; a green solution of copper nitrite is formed which is then decomposed by nitric acid to reproduce nitrous acid:



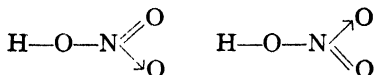
The nitric oxide reduces nitric acid to nitrous acid, and nitric oxide is evolved only at a certain concentration of nitrous acid.

The yellow nitric acid containing NO_2 , when freshly distilled from potassium nitrate and sulphuric acid, does not usually dissolve copper foil unless a little water is added, when nitrous acid is formed and the copper dissolves with violent evolution of red fumes of oxides of nitrogen.

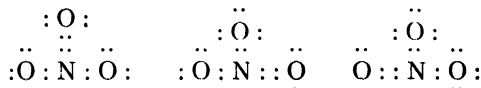
The electronic formula of nitric acid is :



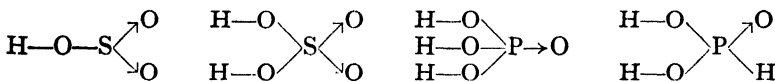
The double bond and the co-ordinate link, however, actually interchange very rapidly by an electron pair shifting from one bond to the other, so that each bond has on the average some double bond and some single bond character. This process occurs in each molecule and all the molecules are identical. A redistribution of valency electrons of this kind is called **resonance**, and the nitric acid molecule should be formulated as a **resonance hybrid**:



In the nitrate ion all three bonds are identical as a result of resonance :



Although oxyacids have been formulated with co-ordinate links to oxygen :

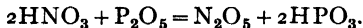


the bond lengths correspond more nearly to those of double bonds, so that the formulation with these is adopted in this book.

Nitrogen pentoxide.—Nitrogen pentoxide was discovered by Deville (1849) by the action of dry chlorine on gently heated silver nitrate :

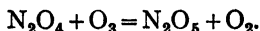


It is prepared by distilling concentrated nitric acid with phosphorus pentoxide :



The mixture is best distilled in a current of ozonised oxygen and the gas passed through a phosphorus pentoxide tube : pure crystals of N_2O_5 are obtained by cooling the gas with solid carbon dioxide and ether.

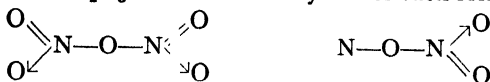
Crystalline nitrogen pentoxide is formed by passing ozonised oxygen into cooled liquid nitrogen tetroxide :



Nitrogen pentoxide forms white very hygroscopic crystals, stable below 0° but decomposing slowly at the ordinary temperature even in

sealed tubes and becoming yellow: $2\text{N}_2\text{O}_5 = 2\text{N}_2\text{O}_4 + \text{O}_2$. They melt with decomposition on heating to a dark-brown liquid, which decomposes into red NO_2 and oxygen at 50° . If suddenly heated the crystals explode. They dissolve with a hissing noise in water forming nitric acid $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3$. Phosphorus and potassium burn in the liquid pentoxide if slightly warmed; charcoal does not decompose it even on boiling, but burns brilliantly if previously ignited. A crystalline compound $\text{N}_2\text{O}_5 \cdot 2\text{HNO}_3$ is formed on cooling a solution of the anhydride in concentrated nitric acid.

The structure of N_2O_5 is a resonance hybrid of such forms as



Manufacture of nitric acid by the arc process.—Formerly, nitric acid was manufactured in Norway from the air by a process based on the reactions described on p. 475. In this, air is blown through a flat circular furnace (Fig. 205), in which an alternating current electric arc burning between water-cooled copper poles is spread out by an electro-magnet into an apparent disc, the temperature of which is about 3000° . In this flame, combination between the oxygen and nitrogen occurs: $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$. The gases after cooling to "freeze" the equilibrium leave the furnace containing 1 per cent. of NO , and pass to a tubular boiler where they are cooled with production of steam.

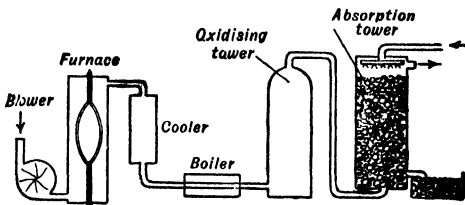


FIG. 205.—Diagram of the arc process.

Formation of nitrogen dioxide begins: $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$; this is a somewhat slow process since it involves the collision of three molecules, and to give time for the reaction the gases pass through an empty oxidising tower, and then to absorption towers built of granite slabs and packed with broken quartz over which water is circulated. In these towers dilute nitric acid is formed:

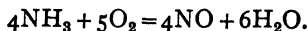


This is concentrated by distilling with concentrated sulphuric acid, or neutralised with limestone to form a solution of calcium nitrate which is evaporated to form a solid fertiliser.

The arc process is now obsolete and nitric acid is at present made by the catalytic oxidation of synthetic ammonia (p. 473).

The oxidation of ammonia.—In 1788 the Rev. Isaac Milner, President of Queens' College Cambridge, found that ammonia when passed over heated manganese dioxide is oxidised to red fumes which on dissolving in water form nitric acid. The French chemist Kuhlmann in 1839 found

that ammonia can be oxidised by passing it mixed with excess of air over heated platinum as a catalyst (see p. 469) :



The colourless gas on cooling becomes red from further oxidation of the nitric oxide :



The best results are obtained when the gas passes very rapidly over the catalyst ; with a slow current much free nitrogen is produced. A mixture of 1 vol. of purified ammonia gas and 7.5 vols. of air filtered from dust is preheated to about 500° by the heat of reaction in a counter-current apparatus (*cf.* p. 562), and is passed through a converter (Fig. 206) containing

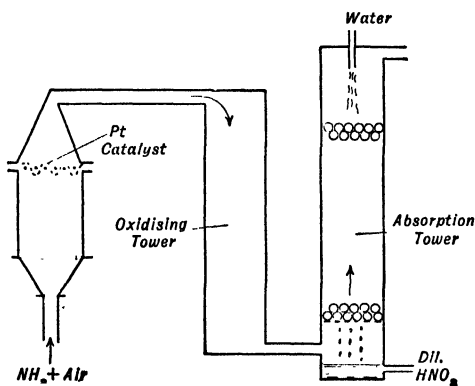
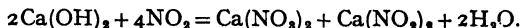


FIG. 206.—Diagram of ammonia oxidation process.

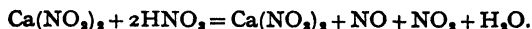
two fine platinum gauzes in contact, when the exothermic reaction proceeds automatically. More than 90 per cent. of the ammonia is oxidised to nitric oxide and 1 sq. ft. of double catalyst will produce $1\frac{1}{2}$ tons of HNO_3 in 24 hours. (The rate of conversion is much greater with a mixture of ammonia and oxygen $\text{NH}_3 + 2\text{O}_2$ with sufficient steam to render it non-explosive, and nitric acid may then be obtained directly by cooling the gas from the converter.) The

exit gases from the converter, containing NO , N_2 , O_2 and steam, are cooled and passed into packed stainless steel towers through which water circulates. Formation of nitric acid occurs as in the arc process (p. 483). The cooled gas may also be compressed by pumps at 100 lb. pressure into stainless steel tanks containing water, when absorption is much more rapid. Most of the nitric acid now manufactured is made by the catalytic oxidation of synthetic ammonia.

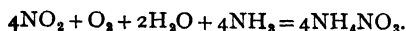
If the cooled oxidised gas is passed through milk of lime, calcium nitrate and nitrite are produced :



When all the lime is neutralised, nitric acid is formed in the solution by reactions previously explained. This decomposes the nitrite with evolution of oxides of nitrogen, which are fully oxidised to NO_2 by air and passed into another absorber of milk of lime :



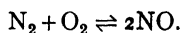
If ammonia gas mixed with air is blown into the cooled and fully oxidised gas from the oxidation apparatus, solid ammonium nitrate is deposited as a powder :



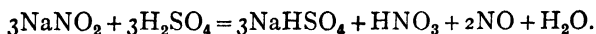
NITRIC OXIDE

History.—Although nitric oxide was obtained by Mayow, Hales and Cavendish, it was first recognised as a distinct gas by Priestley (1772), who prepared it by the action of diluted nitric acid on copper or mercury and called it *nitrous air*.

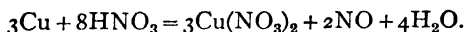
Preparation.—Nitric oxide is formed in small quantities at very high temperatures by the direct combination of oxygen and nitrogen :



It is evolved by dropping concentrated sulphuric acid into sodium nitrite solution :

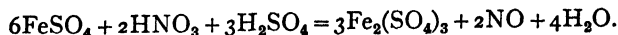


It is usually prepared in the laboratory by the action of diluted nitric acid on copper :

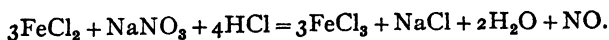


Copper turnings are placed in a flask and a mixture of equal volumes of concentrated nitric acid and water poured in through a thistle funnel. At first the air in the flask becomes red, due to the action of the nitric oxide on atmospheric oxygen : $2\text{NO} + \text{O}_2 = 2\text{NO}_2$. The gas then becomes nearly colourless but slightly yellow since a little NO_2 is produced. This is removed by passage through water and the jars fill with a colourless gas. The gas, especially in the later stages of the reaction, contains variable amounts of nitrogen and nitrous oxide. It may be purified by passing into a cold saturated solution of ferrous sulphate. A nearly black liquid is formed containing $\text{FeSO}_4 \cdot \text{NO}$, which on gentle heating evolves *nearly* pure nitric oxide. The gas so purified still contains 1/500 of its volume not absorbed by fresh ferrous sulphate.

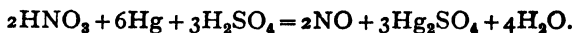
Nearly pure nitric oxide may be obtained by heating a mixture of potassium nitrate, ferrous sulphate, and dilute sulphuric acid. A dark solution of NO in ferrous sulphate is formed which breaks up on heating :



A solution of ferrous chloride mixed with hydrochloric acid and heated with sodium nitrate may also be used :



Very pure nitric oxide is obtained (W. Crum, 1847) by shaking mercury in a flask with concentrated sulphuric acid to which nitric acid or a nitrate has been added :



This reaction is used in the estimation of nitrites or nitrates, or of oxides of nitrogen in commercial sulphuric acid. The solid substance is dissolved in the least amount of water and passed into the Lunge's nitrometer (Fig. 207), a graduated tube *A* with a stopcock *B* communicating with a small cup *C* and an outlet tube *D*, the tube *A* being filled with mercury poured in through a levelling tube *E*. Concentrated sulphuric acid is then introduced and the mixture shaken vigorously with the mercury. The volume of nitric oxide is read off.

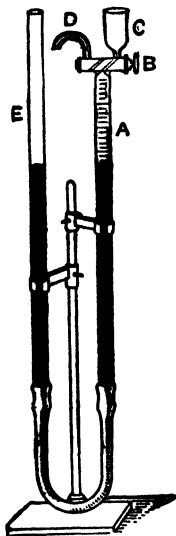
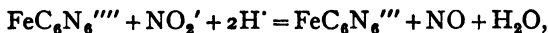
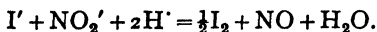


FIG. 207.—Lunge's nitrometer.

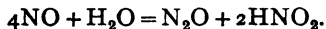
Pure nitric oxide is also prepared by dropping a solution of sodium nitrite and potassium ferrocyanide into dilute acetic acid :



and by the action of sodium nitrite solution on an acidified solution of potassium iodide :



The pure gas should be collected over mercury as it acts slightly on water, evolving traces of nitrous oxide :



Properties.—Nitric oxide is a colourless gas slightly heavier than air and only sparingly soluble in water. It is neutral in reaction. It is difficult to liquefy; the liquid has a somewhat darker blue colour than liquid oxygen and freezes in liquid air to a solid of the same colour.

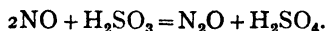
Nitric oxide is freely soluble in cold ferrous sulphate solution forming a black liquid observed by Priestley. The nitric oxide is readily evolved on heating.

The maximum absorption corresponds with $\text{FeSO}_4 \cdot \text{NO}$ and Manchot formulates the black compound as $[\text{Fe}(\text{NO})]\text{SO}_4 \rightleftharpoons \text{FeNO}'' + \text{SO}_4''$. The cation carries the nitric oxide on electrolysis.

Liquid or compressed nitric oxide slowly decomposes into nitrous oxide and nitrous anhydride: $4\text{NO} = \text{N}_2\text{O} + \text{N}_2\text{O}_3$, and hence becomes blue (the colour of N_2O_3). This reaction slowly occurs in presence of water (see above) and especially of alkali solution :



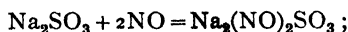
Nitric oxide dissolves only in traces in concentrated sulphuric acid. Sulphurous acid reduces it fairly easily to nitrous oxide :



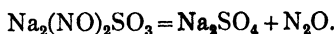
Nitric oxide is *slowly* absorbed by acid permanganate solution, which oxidises it to nitric acid :



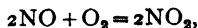
It is not absorbed by alkali (see above) but dissolves *readily* in an alkaline solution of sodium sulphite to form a **nitrososulphate** :



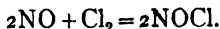
when acidified this is decomposed and *nitrous* oxide is evolved :



Nitric oxide combines with oxygen to form red nitrogen dioxide gas :



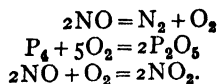
and with chlorine to form **nitrosyl chloride** gas :



Nitric oxide is absorbed by concentrated nitric acid to form a yellow solution of NO_2 : $2\text{HNO}_3 + \text{NO} \rightleftharpoons 3\text{NO}_2 + \text{H}_2\text{O}.$

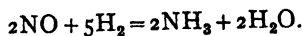
Some combustible substances burning freely in air continue to burn in nitric oxide. Nitric oxide is the most stable oxide of nitrogen : it begins to decompose appreciably into nitrogen and oxygen only above 1000° . The substances probably burn in the oxygen liberated.

A lighted taper, burning sulphur and charcoal, and feebly burning phosphorus are extinguished, but the combustion of brightly burning phosphorus continues brilliantly, a red gas being produced as well as white clouds of phosphorus pentoxide :



A mixture of carbon disulphide vapour and nitric oxide, formed by shaking a few c.c. of carbon disulphide in a jar of nitric oxide, burns when kindled with a brilliant blue flame.

A mixture of hydrogen and nitric oxide when passed over heated platinum is reduced to ammonia :



The composition of nitric oxide* may be found by heating a piece of potassium (sodium does not react) in the gas in a bent tube over

* It should be noted that nitric oxide does not easily explode when sparked with hydrogen unless it is mixed with nitrous oxide (see p. 490).

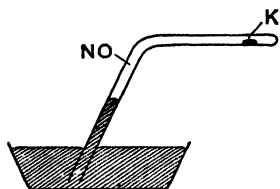


FIG. 208.—Composition of nitric oxide.

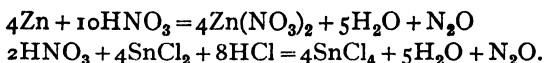
mercury (Fig. 208), or a spiral of iron wire may be heated strongly by an electric current in nitric oxide in a cylinder over water. The oxygen is removed by the potassium or the iron and after cooling the residual nitrogen occupies half the volume of the nitric oxide taken.

Thus one molecule of nitric oxide contains half a molecule or one atom of nitrogen and the formula is NO_x . The density shows that the molecular weight is 30 and hence the weight of oxygen in a molecule of nitric oxide is $30 - 14 = 16$ or one atom. Hence the formula is NO .

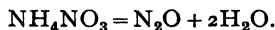
NITROUS OXIDE

History.—Priestley in 1772 noticed that when nitrous air (NO) stands in contact with moist iron filings or liver of sulphur, it contracts like common air but the residual gas supports combustion better than common air. Priestley called the gas *dephlogisticated nitrous air*. It was carefully examined by Davy in 1799. He prepared it nearly pure by a method discovered by Berthollet in 1785, viz. by heating ammonium nitrate, determined its composition and examined its physiological action. He called it nitrous oxide.

Preparation.—Nitrous oxide is formed in a rather impure state by the reduction of moist nitric oxide by sulphur dioxide or sulphites (p. 487), and by the reduction of dilute nitric acid by zinc or stannous chloride :



In the laboratory and on the technical scale nitrous oxide is prepared by the decomposition of ammonium nitrate by careful heating :



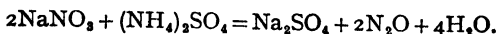
About 50 gm. of previously dried ammonium nitrate is gently heated in a flask or retort over wire gauze. The salt melts and begins to decompose below 200° . The reaction is exothermic and above 250° the salt is liable to explode ; before this occurs nitric oxide, nitrogen and ammonia are evolved.

The gas is purified from nitric oxide and higher oxides of nitrogen by passing through potassium dichromate or permanganate solution, from chlorine (derived from ammonium chloride in the ammonium nitrate) and nitric acid vapour by sodium hydroxide solution, and from ammonia by concentrated sulphuric acid, and is collected over warm water or mercury.

It may be dried by calcium chloride or sulphuric acid and collected by downward displacement. It may contain a few per cent. of nitrogen :

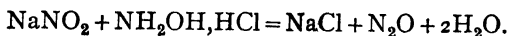


A mixture of sodium nitrate and ammonium sulphate may be used instead of ammonium nitrate :

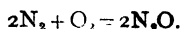


Nitrous oxide prepared by heating ammonium nitrate and carefully purified is used as an anaesthetic ; it is liquefied by compression in steel cylinders.

Very pure nitrous oxide is obtained by gently warming a solution of equimolecular amounts of sodium nitrite and hydroxylamine hydrochloride :



Nitrous oxide is formed with some difficulty by direct synthesis : an electric discharge is passed through nitrogen at low pressure in a silica tube the walls of which are previously saturated with oxygen by passing a discharge through that gas in the tube :



Properties.—Nitrous oxide is a colourless gas with a faint sweetish odour and taste, and is about $1\frac{1}{2}$ times as heavy as air. It is appreciably soluble in water (0.78 vol. in 1 vol. of water at 15°) and more soluble in alcohol.

The aqueous solution is neutral to litmus and nitrous oxide is a neutral oxide. The gas is fairly easily liquefied by compression and forms a colourless mobile liquid. When cooled in liquid air or when *rapidly* evaporated (not spontaneously on reducing the pressure, as in the case of liquid carbon dioxide) the liquid freezes to a white solid.

Nitrous oxide supports combustion more vigorously than air, since it yields on decomposition a gas containing one-third of its volume of oxygen as compared with one-fifth in air : $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$. Decomposition of nitrous oxide begins at 520° and is complete at 900° (nitric oxide is stable to 1000°). The gas is decomposed by sparks ; some nitric oxide is also formed. Combustion in *nitric* oxide when it begins is more brilliant than in nitrous oxide.

A taper burns in nitrous oxide with a brilliant flame and charcoal burns and a glowing chip is rekindled as in oxygen.* Nitrous oxide is distinguished from oxygen by its smell, its greater solubility in water, and the fact that (when pure) it does not produce a red gas with nitric oxide.

* The gas collected over warm water is often too moist to show satisfactory combustion reactions ; that taken from a cylinder of liquid nitrous oxide is satisfactory. The gas may also be dried and collected by displacement.

Brightly burning phosphorus burns in nitrous oxide with a brilliant flame, producing clouds of phosphorus pentoxide and a little red nitrous dioxide. Feebly burning sulphur is extinguished, but if brightly burning the sulphur continues to burn vigorously with a double flame: an outer large flickering yellow flame and an inner bright blue flame. Sodium and potassium when heated burn in the gas to form peroxides, and iron wire burns as in oxygen. A hydrogen flame is greatly enlarged in nitrous oxide.

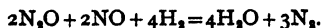
Gay-Lussac and Thenard found the composition of nitrous oxide by heating potassium in a measured volume of the gas confined in a bent tube over mercury (p. 488). After cooling an equal volume of nitrogen remained. The gas may also be decomposed by heated iron wire, as in the case of nitric oxide.

These experiments show that *nitrous oxide contains its own volume of nitrogen, i.e.* one molecule of nitrous oxide contains one molecule of nitrogen, or the formula is N_2O_x . The density of the gas corresponds with a molecular weight of 44. But this contains a molecular weight of nitrogen N_2 of weight 28 and therefore $44 - 28 = 16$ parts or one atom of oxygen. Hence $x = 1$ and the formula is N_2O .

Nitrous oxide is an *endothermic* compound and is decomposed into its elements by the shock of exploding mercury fulminate. If mixed with detonating gas ($2H_2 + O_2$) nitrous oxide is also completely decomposed on explosion. Two vols. of nitrous oxide when mixed with electrolytic gas and exploded leave 3 vols. of gas (all the electrolytic gas is condensed to liquid water). On treatment with alkaline pyrogallol, 1 vol. of oxygen is absorbed, and 2 vols. of nitrogen are left.

The formula may also be found by exploding the gas with hydrogen in a eudiometer (Davy, 1799). If 20 c.c. of nitrous oxide are mixed with 20 c.c. of hydrogen and exploded, 20 c.c. of nitrogen are left. The hydrogen must have combined with 10 c.c. of oxygen to form liquid water, so that in 2 vols. of nitrous oxide 2 vols. of nitrogen are combined with 1 vol. of oxygen, and the formula is N_2O . This is *confirmed* by the density.

Nitric oxide does not easily explode with hydrogen, but if mixed with an equal volume of nitrous oxide both gases explode when the mixture is sparked with an equal volume of hydrogen: *

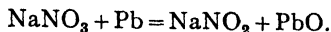


Nitrous acid.—Scheele in 1774 found that the residue left after heating nitre effervesced with acids and gave a red gas, hence he concluded that it was a salt of a new acid: it is *potassium nitrite*:



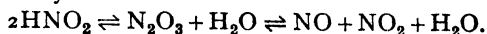
* See Partington and Stratton, *Intermediate Chemical Calculations*, p. 37.

The reduction occurs at a lower temperature by fusing potassium or sodium nitrate with lead or copper :

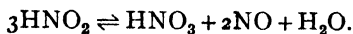


If a dilute acid, even acetic, is added to a nitrite solution free **nitrous acid** HNO_2 is formed but decomposes, oxides of nitrogen being liberated. The solution has a pale blue colour, not due to nitrous acid but to **nitrous anhydride** N_2O_3 , which has a deep blue colour in the liquid state.

The mode of decomposition of the nitrous acid in fairly concentrated solutions is probably :



In dilute solutions it decomposes according to the equation :

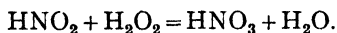


The amount of nitrous acid or its anhydride left in aqueous solution never exceeds a few per cent. A pure dilute solution of nitrous acid is obtained by precipitating a solution of barium nitrite with dilute sulphuric acid ; it is pale blue in colour and slowly decomposes, especially on heating or shaking, with evolution of nitric oxide. The free acid can be titrated with standard alkali and alizarin red as indicator (it reacts with methyl orange).

Nitrous acid and nitrites are *reducing* agents : $\text{HNO}_2 + \text{O} = \text{HNO}_3$; they reduce permanganates and chromates. They may be estimated by running the solution into excess of warm acidified $N/2$ potassium permanganate, and titrating the excess with standard oxalic acid :



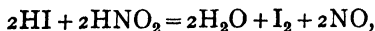
They are also oxidised by hydrogen peroxide :



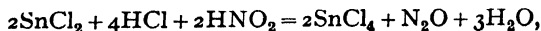
Nitrous acid and nitrites sometimes act as *oxidising* agents :



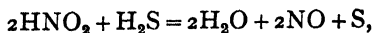
Iodine is liberated from acidified potassium iodide :



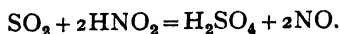
indigo is bleached, stannous chloride is oxidised to stannic chloride :



sulphur is precipitated from hydrogen sulphide :



and sulphur dioxide is oxidised to sulphuric acid (cf. p. 487) :



In presence of atmospheric oxygen NO will reproduce nitrous acid, so

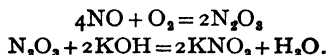
that a small amount of nitrous acid may effect a considerable amount of oxidation by acting as a carrier of oxygen, *i.e.* as a catalyst.

The liberation of iodine from potassium iodide (blue colour with starch) is a test for nitrous acid or a nitrite in acid solution. Still more delicate tests are (i) the brown colour with a solution of metaphenylenediamine hydrochloride in hydrochloric acid, and (ii) the intense pink colour with a mixture of solutions of sulphanilic acid and α -naphthylamine in acetic acid. These two reactions may be used for the estimation of nitrites in water.

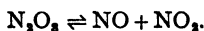
Nitrites detonate violently when heated with thiosulphates or cyanides, so that care must be used in heating solid mixtures of nitrates with reducing substances which can form these bodies. A mixture of sulphur, potassium carbonate and nitre, or of nitre and potassium cyanide, detonates *violently* when heated. These mixtures are sometimes met with in qualitative analysis.

NITROUS ANHYDRIDE OR DINITROGEN TRIOXIDE

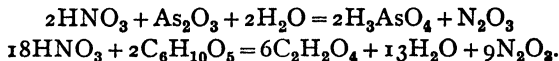
History.—Red vapours of higher oxides of nitrogen were known to the alchemists. Gay-Lussac (1816) found that when 4 vols. of nitric oxide and 1 vol. of oxygen are mixed over potassium hydroxide solution the gas is completely absorbed and a nitrite is formed :



By cooling the mixed gases an indigo-blue liquid is formed, but on evaporation the N_2O_3 dissociates almost completely into nitric oxide and nitrogen dioxide :



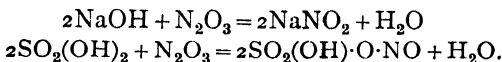
Preparation.—Dinitrogen trioxide is most conveniently prepared by heating fairly concentrated nitric acid with arsenious oxide or starch, which act as reducing agents. The deep red gas is liquefied by cooling. The arsenious oxide is oxidised to arsenic acid; starch is oxidised to oxalic acid :



About 100 gm. of white arsenic are heated with 80 c.c. of nitric acid of sp. gr. 1.35 (56 per cent. HNO_3) in a large flask with a long tube bent slightly backward and connected by a paraffined cork with a glass worm cooled with ice and salt (Fig. 209). A deep blue liquid condenses and is collected in a tube contained in ice and salt. The tube may be sealed off to preserve the liquid. *Vapours of higher oxides of nitrogen are dangerously poisonous.*

The composition of the gas is determined by decomposing it by passing over copper turnings heated to *bright* redness, when copper oxide is formed and nitrogen passes on.

The gas is absorbed by sodium hydroxide solution to form sodium nitrite, and by concentrated sulphuric acid to form nitroso-sulphuric acid. It therefore behaves chemically as if it were nitrous anhydride N_2O_3 :

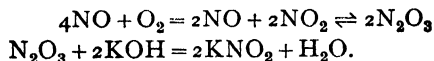


The vapour density shows, however, that it is a mixture of equal volumes of nitric oxide and nitrogen dioxide, so that N_2O_3 is almost completely dissociated into NO and NO_2 . About 5 per cent. by volume of N_2O_3 is present in the gas at room temperature (Dixon and Peterkin, 1899).

If the blue liquid is dried by prolonged exposure to phosphorus pentoxide it may be volatilised without decomposition and has a vapour density corresponding with N_4O_6 , but in presence of the least trace of moisture it decomposes: $N_4O_6 = 2NO + 2NO_2$. (H. B. and M. Baker, 1907).

Liquid nitrous anhydride is obtained by the action of nitric oxide on solid nitrogen dioxide cooled in liquid air. It is not oxidised to NO_2 by oxygen below -100° and (unless quite dry) begins to decompose at -21° .

A mixture of nitric oxide with oxygen or air, if rapidly made in presence of alkali, is quickly absorbed with formation of nitrite only and thus behaves as if it contained N_2O_3 ;



The mixture of gases, if first allowed to stand, is more slowly absorbed by alkali with formation of both nitrite and nitrate; the nitric oxide is then completely oxidised to nitrogen dioxide before absorption:

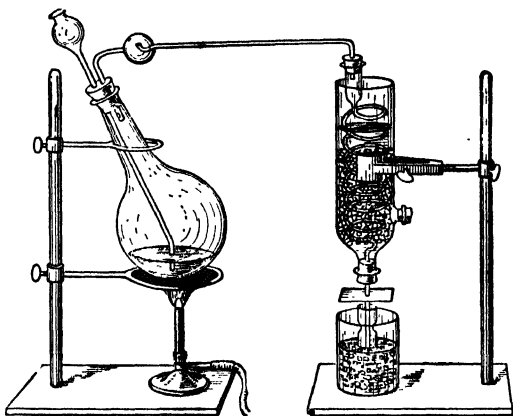
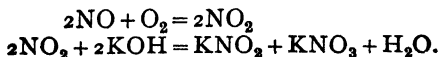
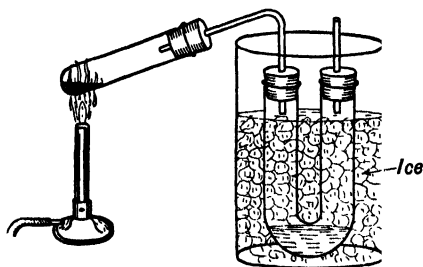


FIG. 209.—Preparation of nitrous anhydride.

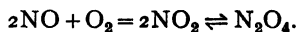
NITROGEN DIOXIDE AND DINITROGEN TETROXIDE

History.—Dulong (1816) by mixing 2 vols. of nitric oxide with 1 vol. of oxygen and cooling in a freezing mixture the deep red gas formed obtained liquid nitrogen dioxide NO_2 (or N_2O_4). It was called "nitrogen peroxide" by Graham.

Preparation.—If a dry mixture of 1 vol. of oxygen and 2 vols. of nitric oxide is passed *slowly* through a large bulb so as to allow time for complete oxidation, and the gas



then passed through a spiral tube cooled in a freezing mixture, yellow liquid nitrogen tetroxide is condensed:



Since this is a termolecular reaction the final stage is rather slow and if the gas is condensed

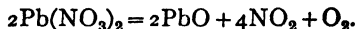
FIG. 210.—Preparation of nitrogen dioxide.

too rapidly a green liquid (containing N_2O_3) is formed. It is curious that the velocity of this gas reaction *decreases* with rise of temperature, which seems to show that some unstable intermediate product, perhaps N_2O_3 , is formed.

Nitrogen dioxide is evolved by the action of *concentrated* nitric acid on copper or bismuth (Priestley):



but this product is impure. Nitrogen dioxide is usually prepared by the decomposition of dry lead nitrate by heat:



Dry powdered lead nitrate is heated in a hard glass tube and the gas evolved is passed through a U-tube cooled in a mixture of ice and salt (Fig. 210). A yellow liquid collects. A glowing chip held over the exit of the U-tube bursts into flame, showing that oxygen is also evolved. If the N_2O_4 is poured on crushed ice in a test-tube a deep blue layer rich in N_2O_3 separates (Fritzsche, 1840):

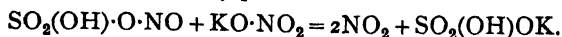


A more satisfactory method of preparing nitrogen dioxide in quantity is the action of nitric acid and phosphorus pentoxide on nitrous anhydride (Cundall, 1891): $\text{N}_2\text{O}_3 + 2\text{HNO}_3 \rightleftharpoons 2\text{N}_2\text{O}_4 + \text{H}_2\text{O}.$

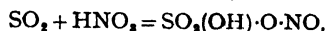
To the blue liquid obtained by distilling nitric acid with arsenious oxide excess of P_2O_5 is added and then fuming nitric acid drop by drop

until the colour changes to yellow. The mixture should be kept well cooled during the reaction. The liquid is distilled off through a worm tube cooled in ice, rejecting the first few c.c. which are coloured green. It is collected in a tube immersed in ice, and sealed off.

Pure nitrogen dioxide is obtained by heating nitrososulphuric acid ("chamber crystals") with dry potassium nitrate :



Sulphur dioxide is *slowly* passed into 25 c.c. of fuming nitric acid in a stoppered retort well cooled in a freezing mixture. When the acid is converted into a pasty mass of chamber crystals :



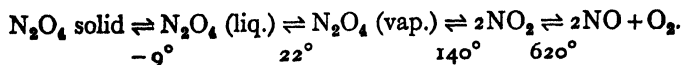
60 gm. of dry powdered potassium nitrate is added, the substances are mixed with a glass rod, and the nitrogen dioxide distilled off by gently heating.

Properties.—Nitrogen dioxide in a *good* freezing mixture solidifies to pale yellow nearly colourless crystals, melting at -9° to a honey-yellow liquid. The solid probably consists almost entirely of N_2O_4 , which appears to be colourless. The liquid at the melting point already contains some NO_2 , which is strongly coloured. On warming, the colour deepens to yellow, orange and reddish-brown and the liquid boils at 22° giving a red vapour. The colour of the vapour darkens on further heating, as may be seen by comparing two globes containing it, one at the ordinary temperature ; at 40° is almost black in colour.

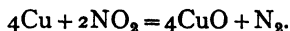
The colour change on heating at atmospheric pressure is accompanied by a decrease in vapour density up to 140° , when the density becomes constant and corresponds with NO_2 : the intermediate densities correspond with the dissociation : $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$.

Temperature	Vapour density	Percentage dissociation
22° (b. pt.)	39.81	15.7
27	38.3	20.1
60	30.1	52.8
100	24.3	89.3
135	23.1	99.1
140	22.96	100.0

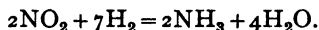
Above 140° , the vapour density further decreases but the colour becomes paler, until at 620° the gas is colourless owing to dissociation into nitric oxide and oxygen : $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$. Recombination occurs in the reverse order on cooling :



The composition of nitrogen dioxide is found by passing it over copper heated to *bright redness* (otherwise NO is formed) :



Nitrogen dioxide vapour does not readily support the combustion of a taper, but strongly burning phosphorus and carbon burn in it. The gas is probably decomposed into nitrogen and oxygen, or nitric oxide and oxygen. Potassium inflames spontaneously in the gas; heated sodium burns in it; and a spiral of heated iron wire combines with the oxygen, leaving half the volume of nitrogen: $2\text{NO}_2 = \text{N}_2 + 2\text{O}_2$. Tin is oxidised to the dioxide, lead to the monoxide ($\text{Pb} + \text{NO}_2 = \text{PbO} + \text{NO}$); carbon monoxide to the dioxide at the ordinary temperature ($\text{NO}_2 + \text{CO} = \text{NO} + \text{CO}_2$); hydrogen sulphide deposits sulphur ($\text{NO}_2 + \text{H}_2\text{S} = \text{NO} + \text{H}_2\text{O} + \text{S}$). A mixture of the gas and hydrogen is reduced to ammonia on passing over heated platinum :



Nitrogen dioxide is absorbed by concentrated sulphuric acid with formation of nitrososulphuric acid and nitric acid, and since these substances decompose each other a state of equilibrium is attained: $\text{N}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_2(\text{OH}) \cdot \text{O} \cdot \text{NO} + \text{HNO}_3$. The gas is rather slowly absorbed by alkalis with formation of an equimolecular mixture of nitrite and nitrate: $2\text{KOH} + \text{N}_2\text{O}_4 = \text{KNO}_2 + \text{KNO}_3 + \text{H}_2\text{O}$.

The atomic weight of nitrogen has been found by indirect methods which involve a knowledge of other atomic weights (p. 76), notably from

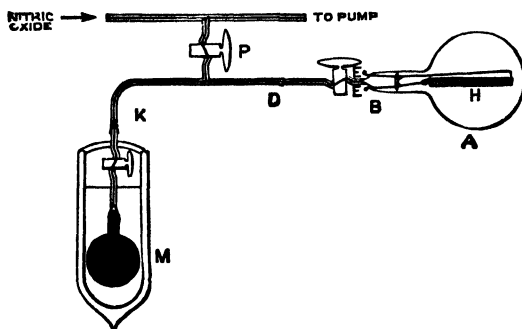


FIG. 211.—Gray's apparatus for determining the composition of nitric acid.

the ratio $\text{Ag} : \text{AgNO}_3$ which assumes $\text{Ag} = 107.88$. Several determinations from gas densities have been made and some accurate analyses of gaseous oxides of nitrogen.

An accurate analysis of nitric oxide by heating finely-divided nickel in the gas was made by R. W. Gray (1905). The gas was contained in a

bulb *A* (Fig. 211) which was weighed empty and then full of gas. The platinum boat *H* heated by a platinum spiral contained the nickel. When decomposition was complete: $2\text{Ni} + 2\text{NO} = 2\text{NiO} + \text{N}_2$, the bulb *A* was connected with the vacuous bulb *M* containing charcoal and cooled in liquid air. The nitrogen was adsorbed by the charcoal and was weighed. The increase in weight of *A* gave the weight of oxygen. The ratio $\text{N}:\text{O} = 14.0085:16$ was found. The density of NO was found to be 1.3402 and after correction for deviation from Boyle's law (p. 83) the molecular weight was calculated as 30.009, hence $\text{N} = 30.009 - 16.000 = 14.009$. The limiting density of nitrogen gave the value 14.008.

CHAPTER XXIX

PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH

PHOSPHORUS

History.—Phosphorus was discovered about 1674 by Brand,* who obtained it by strongly heating the residue from evaporated urine, which contains phosphates and carbon. It excited great interest because of its phosphorescence. Kunckel in 1676 independently discovered phosphorus. Brand sold the secret of preparation to Krafft, who showed phosphorus to Boyle and gave him a hint of the source. Boyle discovered many of the important properties of phosphorus, and published the preparation in 1681; it was made in London for many years by his assistant Hanckwitz. Gahn about 1770 discovered calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ in bones, and Scheele prepared phosphorus from bone-ash. The process formerly in use for the preparation of phosphorus from bone-ash was devised by Scheele in 1777. The elementary nature of phosphorus was recognised by Lavoisier in 1777.

Occurrence.—Phosphorus always occurs in the combined state. The primary mineral appears to be *apatite* $\text{CaF}_2, 3\text{Ca}_3(\text{PO}_4)_2$; *chlorapatite* $\text{CaCl}_2, 3\text{Ca}_3(\text{PO}_4)_2$ also occurs. These are practically insoluble in dilute acids. From them by weathering the secondary deposits of phosphates have probably been formed, although many of these consist of fossil bones, in the formation of which the phosphates were first assimilated by animals.

The so-called "soft phosphates" are *coprolites* (calcium phosphate of fossil excreta) and *Charleston phosphate* from river beds in South Carolina; they are easily decomposed by sulphuric acid. "Hard" varieties are *estramadurite* and *sombrerite*, which are Spanish minerals; *Redonda phosphate*, a cheap and rich ore from the West Indies, is aluminium phosphate AlPO_4 ; *vivianite* is ferrous phosphate $\text{Fe}_3(\text{PO}_4)_2, 8\text{H}_2\text{O}$. The softer ores are used in the manufacture of superphosphate of lime, a valuable fertiliser (p. 342). The richest phosphate deposits are in North Africa and Florida.

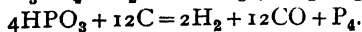
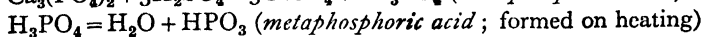
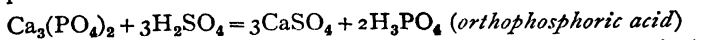
Phosphorus is an essential constituent of vegetable and animal tissues, occurring especially in the seeds, in the yolk of eggs, in the nerves and

* See Partington, "The Discovery of Phosphorus," *Science Progress*, 1936, p. 402.

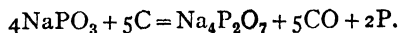
brain, and in bone-marrow, usually in the form of fats containing esters of phosphoric acid known as *lecithins* or *glycero-phosphates*.

Bone-ash contains about 80 per cent. of calcium phosphate with calcium carbonate and a little fluoride. Phosphates in the soil are essential to plant growth and when necessary are supplied by fertilisers.

Preparation.—Phosphorus was formerly prepared from bone-ash or soft mineral phosphates, decomposed by hot sulphuric acid (sp. gr. 1.5) so as to form insoluble calcium sulphate and phosphoric acid. The phosphoric acid was filtered, evaporated to a syrup, mixed with powdered coke and distilled in fireclay retorts at a bright-red heat, when phosphorus vapour came over :

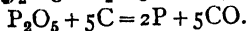
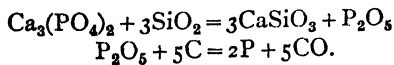


Normal phosphates are not reduced by carbon, but metaphosphates are reduced at high temperatures :



Phosphorus is now made by a method discovered by Wöhler in 1829 but first used industrially by Readman, Parker and Robinson in 1888, viz. the direct reduction of a phosphate by carbon in presence of silica, which forms a silicate and liberates phosphorus pentoxide vapour, which is reduced by the carbon at a high temperature. This method is applicable to hard sparingly-soluble phosphates, since the mineral is not treated with acid.

A mixture of phosphate, sand and coke is fed by a worm-conveyor into a closed electric furnace, provided with an outlet above for the gases and phosphorus vapour, a slag hole below, and carbon electrodes between which an electric arc is struck (Fig. 212). The reaction is purely thermal and no electrolysis takes place :



The cooled gas is passed into water when crude phosphorus condenses as a dark-coloured mass. It is purified by melting and stirring under a dilute solution of chromic acid, when some impurities oxidise and pass into solution and others separate and rise as a scum. The liquid phosphorus may also be filtered by pressing through chamois leather.

R

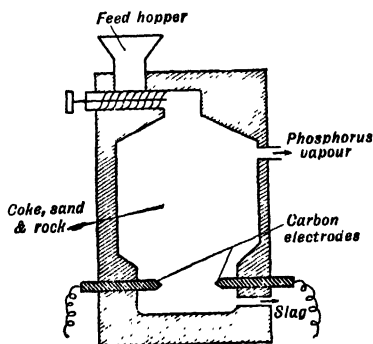


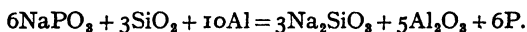
FIG. 212.—Electric phosphorus furnace (diagrammatic).

P.C

The colourless phosphorus is finally cast into wedges (about 2 lb.) in tin moulds, or into sticks by running the liquid into glass tubes cooled in water and drawing out the stick at the other end.

Most of the phosphorus output is used in the manufacture of matches. Some is used in making phosphor-bronze and incendiary and smoke bombs, as a poison for rats, and in the preparation of phosphorus trichloride, pentachloride, and pentoxide.

On the small scale, the production of phosphorus may be shown by strongly heating a mixture of 1 gm. of powdered sodium metaphosphate (obtained by heating microcosmic salt in a crucible) with 0.5 gm. of aluminium powder and 3 gm. of fine white sand in a hard glass tube in a current of dry hydrogen. Phosphorus distils over, condensing in the cool part of the tube :



Phosphorus exists in two main allotropic forms: *white phosphorus* (sometimes called "yellow" phosphorus although it is quite colourless when pure) and *red phosphorus*, which is the only stable form.

White phosphorus.—Ordinary white phosphorus is a translucent white solid like wax, of sp. gr. 1.83. On exposure to light it rapidly becomes yellow. It is soft enough at the ordinary temperature to be cut with a knife—an operation which should always be performed under water. Phosphorus is kept in bottles under water on account of the ease with which it takes fire in air. It has a low melting point (44°). Phosphorus boils at about 290° yielding a colourless vapour the density of which corresponds with P_4 . At very high temperatures the density decreases, indicating partial dissociation: $\text{P}_4 \rightleftharpoons 2\text{P}_2$.

White phosphorus is very sparingly soluble in water but is soluble in benzene, turpentine, olive oil, sulphur chloride, phosphorus trichloride, and especially in carbon disulphide. The elevation of boiling point of the latter solvent gives a molecular formula P_4 agreeing with that of the vapour. On evaporation out of contact with air the solution in carbon disulphide deposits crystals. Large transparent regular crystals with a play of colours like diamonds are formed by the slow sublimation of phosphorus in a vacuum tube, one end being kept cool by a moist cloth. The tube is kept in the dark, since on exposure to light the crystals become red and opaque.

A characteristic property of white phosphorus is the ease with which it undergoes spontaneous oxidation when exposed to air at the ordinary temperature, accompanied by a green glow or phosphorescence. If gently warmed to about 50° it catches fire in dry air and burns with a white flame, forming white fumes of the pentoxide P_2O_5 . Finely-divided

phosphorus takes fire spontaneously in the air. Phosphorus may be burnt under hot water in a current of oxygen.

A solution of phosphorus in carbon disulphide is poured on a piece of blotting-paper supported on a tripod stand; the solvent rapidly evaporates and the finely-divided phosphorus inflames.

A few small pieces of phosphorus are put into a test-tube half filled with water, and the tube is supported in a beaker of hot water. Oxygen is passed in through a tube. The phosphorus melts, takes fire and burns. Some red phosphorus is formed.

White phosphorus burns spontaneously in chlorine and explodes violently in contact with bromine. It combines spontaneously with iodine (p. 12).

Sticks of white phosphorus kept under water in presence of air become covered with a white crust, which is ordinary phosphorus detached by unequal oxidation; it is not formed in water free from air. This crust slowly turns red and the dark colour of the red phosphorus spreads through the mass.

White phosphorus is very poisonous, the lethal dose being about 0.15 gm. Workmen exposed to the vapour are liable to decay of the bones, especially of the jaw ("phossy-jaw") and its use in the manufacture of matches has ceased.

Red phosphorus.—This modification, formerly called "amorphous phosphorus", was prepared by Schrötter in 1845 by heating white phosphorus for a few hours at 250° in a flask filled with nitrogen or carbon dioxide. The liquid deposits a red powder and finally solidifies to a purplish-red mass. The transformation at higher temperatures is reversible. Red phosphorus is also left as a residue when white phosphorus burns in air or in oxygen under water.

Red phosphorus is made by heating about a ton of phosphorus in a large cast-iron pot provided with a cover through which passes an upright iron tube. The pot is carefully and uniformly heated at 240° , the temperature of the fused phosphorus being controlled by thermometers protected by iron tubes, since phosphorus attacks glass (much heat is evolved in the conversion of white into red phosphorus). A little phosphorus burns, absorbing the oxygen from the air in the vessel, and oxidation then ceases. The hard solid left in the pot when the conversion is complete is ground up under water and boiled with a solution of sodium hydroxide to free it from unchanged white phosphorus. It is repeatedly washed with hot water and dried with steam. It usually contains about 0.5 per cent. of white phosphorus and some phosphoric acid.

The colour of red phosphorus varies according to the method of preparation. Some kinds are rather yellow than red, others are bright

sealing-wax red, and the commercial product made by prolonged heating is dark violet-red and has a specific gravity of about 2.34. The colour differences probably depend on the particle size. All the red forms are insoluble in carbon disulphide, are not self-luminous, have no smell or taste and are said to be non-poisonous. On exposure to air very little change occurs although slight oxidation takes place, the dry powder becoming moist and phosphoric acid being formed. The powder does not ignite in air until heated to about 240° and it burns in chlorine only when heated; when strongly heated out of contact with air it is converted into vapour, which on cooling deposits white phosphorus.

A little red phosphorus is put into a hard glass test-tube, fitted with a rubber stopper and two tubes. The air is displaced from the tube by a slow stream of carbon dioxide and the phosphorus heated. Colourless drops of white phosphorus distil on to the cooler portion of the tube.

White phosphorus is a metastable form and passes slowly into red phosphorus even at the ordinary temperature when exposed to light. It is metastable under all conditions and hence phosphorus shows *monotropy* (p. 24). The vapour pressure of white phosphorus is greater than that of red phosphorus, and if white phosphorus is placed in one limb of a U-tube at 324° and red phosphorus at 350° in the other, distillation occurs from the cooler to the hotter position.

Ordinary red phosphorus was once considered to be amorphous but the commercial violet-red form consists of minute rhombohedral crystals.

Almost black crystals of "metallic" phosphorus which are stable in air were obtained by Hittorf in 1865 by crystallising a solution of white phosphorus in molten lead and dissolving out the lead with dilute nitric acid; these crystals also sublime when red phosphorus is heated in a sealed tube at 530° with the upper part of the tube kept at 444° . The crystals do not conduct electricity. Ordinary red phosphorus is probably a stage in the formation of "metallic" phosphorus, but some "scarlet" amorphous phosphorus is probably present, this form being deposited on prolonged boiling of a solution of white phosphorus in phosphorus tribromide. The scarlet phosphorus is chemically more active than ordinary red phosphorus but it oxidises only very slowly in air and is said to be non-poisonous. It dissolves in caustic soda solution and in nitric acid.

A second black modification of phosphorus is formed on heating white phosphorus under very high pressure; it is a fairly good conductor of electricity. Other allotropic forms of phosphorus have also been described. The molecular weight of violet phosphorus is probably P_8 or even higher.

The glow of phosphorus.—The oxidation of white phosphorus when exposed to air is accompanied by the emission of a faint green glow,

white fumes being at the same time evolved. The glow is produced when only minute traces of phosphorus or oxygen are present, and its formation is used as a test for free phosphorus in cases of poisoning.

A small piece of phosphorus is added to water in a flask connected with a Liebig's condenser. On boiling the water, the phosphorus distils over with the steam and a phosphorescent glow is seen in a dark room at the point in the condenser where the vapour deposits liquid.

The glow of phosphorus is shown in the "cold flame" experiment. A few pieces of phosphorus are placed in a dry receiver, which is then filled up with glass wool. The receiver is heated on a water-bath, a stream of dry carbon dioxide being passed through (Fig. 213). The phosphorus vapour carried along with the gas oxidises in the air, and a green flame appears at the top of the exit tube. This is so cool that a finger may be held in it and it will not kindle the head of a match.

The glow of phosphorus was investigated by Boyle, who found that: (1) phosphorus glows only in the presence of air; (2) an acid is produced which differs from phosphoric acid, since it gives little flashes of light on heating [phosphorous acid]; (3) the glow is exhibited by solutions of phosphorus in olive and some other oils, but oils of mace and aniseed prevent it; (4) a very small quantity of phosphorus (1 part in 500,000 parts of water) can be detected by the glow; (5) after long exposure to phosphorus, the air acquires a strong odour [ozone] distinct from the visible fumes.

A little later it was observed that the glow is brighter when the air is rarefied by an air-pump. The glow is extinguished in a Torricellian vacuum so that the presence of a trace of oxygen is necessary. Phosphorus does not glow in ordinary moist oxygen at atmospheric pressure but the glow appears if the pressure of the oxygen is reduced or an inert gas is added. At a *very* low pressure (less than 1 mm.) the glow ceases again. According to Russell (1903) phosphorus glows very feebly at atmospheric pressure in oxygen dried by sulphuric acid, or even at higher pressures if the surface is very clean, lower oxides of phosphorus being produced. At pressures lower than 500 mm. at room temperature the glow in dry oxygen becomes much brighter and phosphorus pentoxide is formed. According to Dixon and Baker (1889) phosphorus does not glow at any pressure in oxygen dried by phosphorus pentoxide. Graham (1829) found that the glow is inhibited by ether, naphtha, or turpentine vapour. (The action of essential oils had been observed by Boyle.)

The effect of pressure on the glow may be shown by pouring a solution of white phosphorus in olive oil into a bolt-head flask fitted with a rubber stopper carrying two delivery tubes. The air is displaced from the flask by oxygen and the clips on the tubes closed. The glow will disappear

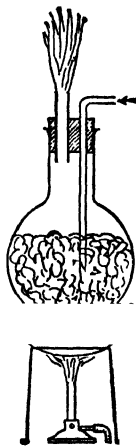


FIG. 213.—"Cold flame."

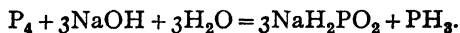
On shaking the oil in the flask and then connecting one tube with an air-pump the glow begins suddenly at a certain lower pressure of oxygen.

Matches.—Formerly white phosphorus was used in making matches but now only red phosphorus and phosphorus sulphide P_4S_3 are used. Common matches have heads containing phosphorus sulphide and an oxidising agent (potassium chlorate) together with an abrasive and glue; they strike on sandpaper when the heat of friction kindles the head. Safety matches are tipped with a paste containing potassium chlorate and other oxidising agents mixed with sulphur, abrasives and glue. The heads contain no phosphorus. They ignite when rubbed on a strip on the box which is covered with red phosphorus, antimony sulphide, abrasive and gum. The wood of matches is steeped in borax, so that it does not glow after the flame is blown out, but is also impregnated with paraffin wax to maintain combustion.

PHOSPHORUS HYDRIDES

Two well-defined hydrides of phosphorus are known, the *gaseous trihydride* called *phosphine* PH_3 (formerly called *phosphoretted* or *phosphuretted hydrogen*) and a *liquid dihydride* P_2H_4 .

Phosphine was obtained by Gengembre in 1783 by boiling white phosphorus with a solution of alkali hydroxide. The colourless gas so obtained is spontaneously inflammable in air. Phosphine and a hypophosphite *e.g.* sodium dihydrogen hypophosphite NaH_2PO_2 , are formed.



A few pieces of white phosphorus are placed in a flask (Fig. 214) containing a 30-40 per cent. solution of sodium hydroxide. The air is displaced

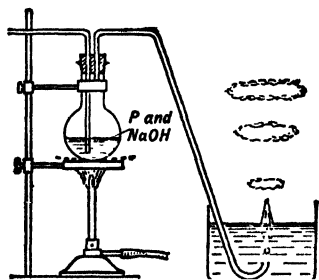
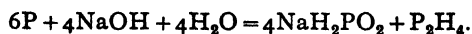


FIG. 214.—Preparation of phosphine. air.

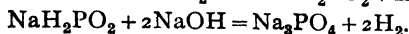
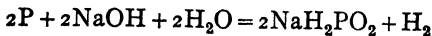
The gas prepared in this way is not pure, as it contains free hydrogen and also the vapour of liquid hydrogen phosphide (P_2H_4), to which it owes its spontaneous inflammability:



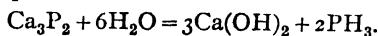
When the gas is passed through a tube cooled in a freezing mixture, or over charcoal, the liquid hydride is condensed and the gas is no longer spontaneously inflammable. The ordinary gas ceases to be spontaneously inflammable when it is mixed with ether vapour.

A gas which is not spontaneously inflammable but contains hydrogen as impurity is formed if phosphorus is heated with alcoholic potash.

The hydrogen present in ordinary phosphine is probably formed by the reactions :



A spontaneously inflammable gas is obtained by the action of water on crude calcium phosphide :



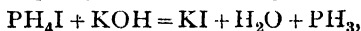
A few pieces of calcium phosphide are dropped into warm water in a beaker and at once covered with a funnel (Fig. 215). The bubbles of gas take fire spontaneously in the air.

Tin canisters filled with calcium phosphide and attached to wooden floats are sometimes used at sea for signalling. The canister is pierced above and below and thrown overboard. The gas ignites spontaneously and burns with a luminous flame (Holmes's signal).

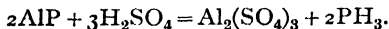
Phosphine which is not spontaneously inflammable is obtained by heating phosphorous acid :



Pure phosphine is prepared by dropping 30 per cent. potassium hydroxide solution on phosphonium iodide (p. 506) :



or by the action of dilute sulphuric acid on aluminium phosphide (prepared by heating aluminium powder and red phosphorus) :



Properties of phosphine.—Phosphine is a colourless gas with an extremely unpleasant odour of decaying fish and is poisonous. It is sparingly soluble in water, alcohol and ether. On heating or sparking it is decomposed into hydrogen and red phosphorus : $2\text{PH}_3 = 2\text{P} + 3\text{H}_2$.

If kindled in a test-tube it burns with deposition of phosphorus ; the heat of combustion of part of the gas decomposes the rest (*cf.* H_2S). A mixture of pure moist phosphine with air or oxygen is not spontaneously explosive, but if the pressure is reduced a violent explosion occurs. Very pure and dry phosphine and oxygen explode at all pressures.

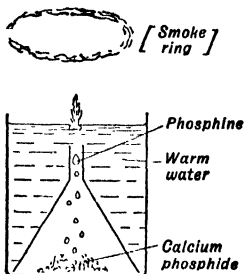
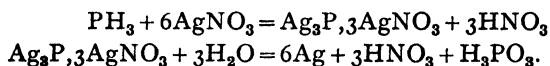


FIG. 215.—Action of water on calcium phosphide.

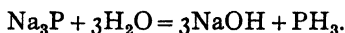
A mixture of phosphine with nitrous oxide explodes when sparked :



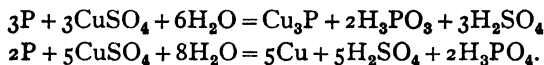
Phosphine ignites spontaneously in chlorine. The pure gas is completely absorbed by a solution of bleaching powder. It precipitates phosphides from solutions of many metallic salts (*e.g.* CuSO_4). These phosphides are also formed by heating the metals with phosphorus or (together with metals) by the action of white phosphorus on solutions of the salts. Phosphine precipitates silver from silver nitrate solution, a yellow intermediate compound being formed (*cf.* AsH_3):



Small pieces of *dry* phosphorus and sodium when heated in a crucible combine with a flash of light forming sodium phosphide Na_3P , which evolves spontaneously inflammable phosphine with water :



A few pieces of white phosphorus immersed in copper sulphate solution slowly become covered with red copper and black copper phosphide, more rapidly on heating :



The formula of phosphine is found by decomposing the gas by continued sparking, when red phosphorus is deposited and 2 vols. of phosphine yield 3 vols. of hydrogen. Hence 1 molecule of phosphine contains $\frac{2}{3}$ molecules or 3 atoms of hydrogen. The density of the gas corresponds with the molecular weight 34, hence it contains $34 - 3 = 31$ parts or 1 atom of phosphorus, and the formula is PH_3 .

Phosphonium compounds.—Although phosphine is neutral to litmus paper it can act as a feeble base, forming with dry halogen hydracids **phosphonium salts** analogous to ammonium salts: $\text{PH}_3 + \text{HX} = \text{PH}_4\text{X}$. A mixture of phosphine and dry hydrogen chloride does not react at atmospheric pressure, but if cooled to -35° or compressed at 15° it deposits white crystals of **phosphonium chloride** which dissociate again on warming or on reducing the pressure: $\text{PH}_3 + \text{HCl} \rightleftharpoons \text{PH}_4\text{Cl}$. **Phosphonium bromide** PH_4Br is more stable and is produced in cubic crystals when a mixture of PH_3 and HBr gas is led into a moderately cooled flask. **Phosphonium iodide** PH_4I is a fairly stable compound formed on mixing PH_3 and HI gas at the ordinary temperature and pressure. It dissociates on heating but the crystals can be sublimed. Phosphonium iodide is at once decomposed by water or alkalis, evolving pure phosphine (p. 505). It is most conveniently prepared by the following process.

10 gm. of white phosphorus are dissolved in an equal weight of carbon disulphide in a tubulated retort. 17.5 gm. of iodine are then added and the carbon disulphide is distilled off on a water bath in a current of CO_2 . The neck of the retort is then connected with a wide glass tube and receiver, and by means of a dropping-funnel fitted in the tubulure of the retort 8.5 gm. of water are dropped gradually on to the phosphorus iodide (Fig. 216). Phosphonium iodide sublimes into the wide tube; the retort is

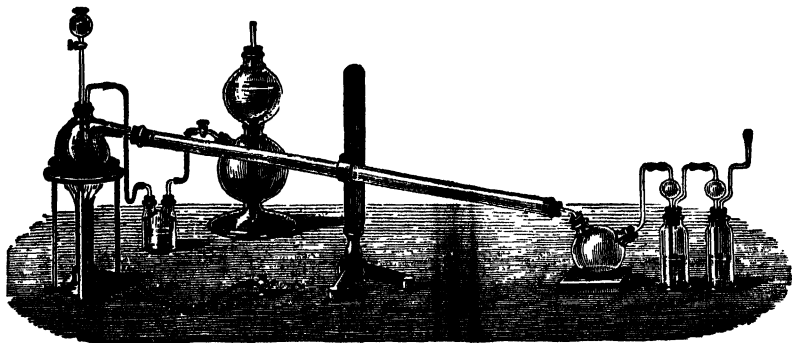


FIG. 216.—Preparation of phosphonium iodide.

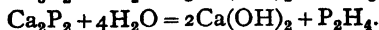
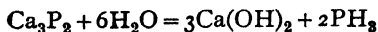
gently warmed at the end of the process. Two wash-bottles containing water are attached to the receiver, to absorb the hydriodic acid also evolved :



Another equation for the reaction is :



Phosphorus dihydride.—This compound is present as vapour in crude phosphine, from which it may be separated as a liquid by cooling. It is formed together with phosphine and amorphous phosphorus by the action of water on *crude* calcium phosphide, formed as a reddish-brown solid containing pyrophosphate $\text{Ca}_2\text{P}_2\text{O}_7$, by passing phosphorus vapour over fragments of quicklime heated to dull redness. Pure calcium phosphide, prepared by heating calcium and phosphorus together under petroleum, gives only phosphine (not spontaneously inflammable) with water, so that the crude product may contain another phosphide Ca_2P_2 or $\text{Ca}=\text{P}-\text{P}=\text{Ca}$:



Pieces of calcium phosphide are dropped through a wide tube into warm water in a Woulfe's bottle (Fig. 217), the air having previously been displaced by hydrogen. The gas is passed through a cooled tube to deposit moisture and the liquid hydride is then condensed to a volatile liquid in a tube cooled in a freezing mixture.

The formula P_2H_4 for this hydride is confirmed by the vapour density below atmospheric pressure. The vapour is unstable and the liquid decomposes on exposure to light, evolving phosphine and depositing a yellow solid

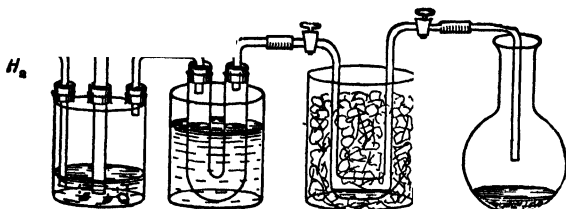
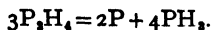


FIG. 217.—Preparation of liquid phosphorus hydride.

formerly regarded as a solid hydride, but probably impure amorphous phosphorus (Royen and Hill, 1936) :

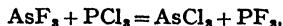


The same solid is formed if the uncondensed vapours from the preparation of the liquid are passed into a large flask containing a little fuming hydrochloric acid.

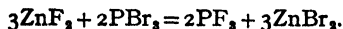
HALOGEN COMPOUNDS OF PHOSPHORUS

Phosphorus forms two series of halogen compounds in which it is 3-valent and 5-valent, respectively: PX_3 and PX_5 .^{*} These are obtained by the direct combination of phosphorus and the halogen, PX_3 or PX_5 being formed according as the former or the latter is in excess. The iodides are PI_3 and P_2I_4 .

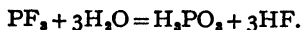
Phosphorus trifluoride PF_3 is a colourless gas obtained by the action of arsenic trifluoride on phosphorus trichloride :



or by warming phosphorus tribromide with zinc fluoride :



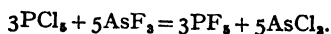
It has no action on glass in the cold and is hydrolysed by water :



A mixture of PF_3 with oxygen explodes on sparking, gaseous phosphorus oxyfluoride POF_2 being formed. Phosphorus oxyfluoride is also obtained by

^{*} Nitrogen shows a maximum covalency of 4, compounds previously formulated as containing 5-valent nitrogen containing a co-ordinate bond. The nitrogen atom cannot be surrounded by more than 8 electrons and as it has 5 already it can take up only 3 from other atoms. If 4 atoms are attached, one must be linked by the lone pair on the nitrogen (see p. 299). Phosphorus, arsenic, antimony and (rarely) bismuth, on the other hand, can form compounds in which their atoms are surrounded by 10 electrons and can thus form true 5-valent compounds. Sulphur in the next group can expand its electron shell to 12, as in SF_6 .

the action of dry HF on P_2O_5 ; it is collected over mercury. The pentafluoride PF_5 is formed when phosphorus burns in fluorine, and when arsenic trifluoride is added to phosphorus pentachloride in a freezing mixture:



The density of the colourless gas corresponds with the formula PF_5 , and this confirms the 5-valency of phosphorus. The gas does not attack glass and fumes in the air forming POF_3 .

Phosphorus trichloride PCl_3 was discovered by Gay-Lussac and Thenard in 1808 and is made by passing dry chlorine over white or red phosphorus heated in a retort and condensing the product in a dry cooled receiver (Fig. 218). It is purified from excess of chlorine by standing over

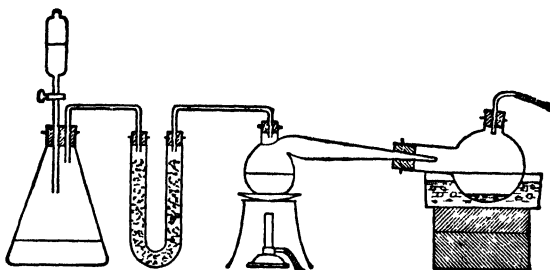
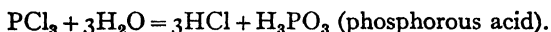


FIG. 218.—Preparation of phosphorus trichloride.

white phosphorus and redistilling. The pure liquid is colourless and may be preserved in a sealed flask. The vapour density corresponds with the formula PCl_3 . The liquid fumes strongly in moist air:



31 gm. of white phosphorus is cut under water into pieces which will pass through the tubulure of a retort; these are dried between filter paper one at a time and inserted by means of crucible tongs into the dry retort previously filled with carbon dioxide. A good cork, carrying a leading-in tube which can be moved, is inserted and connected by rubber tubing with an apparatus evolving dry chlorine, which is passed in, the retort not being heated. (With red phosphorus, heat is necessary.)

The phosphorus burns with a pale flame forming PCl_3 , which distils over. The stream of chlorine must pass rapidly and steadily; if a white sublimate forms (PCl_5) the inlet tube is lowered nearer the phosphorus, whilst if a yellowish-red sublimate forms in the retort the tube is raised.

Phosphorus pentachloride PCl_5 was discovered by Davy in 1810 and is formed by the action of *excess* of chlorine on phosphorus or on phosphorus trichloride:



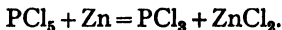
Phosphorus trichloride is dropped *slowly* into a dry flask cooled in ice, through which a current of dry chlorine is passed. A white powder of PCl_5 collects in the flask (Fig. 219).

Phosphorus pentachloride when freshly prepared as above is a white powder but as usually sold it is in pale greenish-yellow crystals. On heating it volatilises without fusion and can be sublimed. The vapour is dissociated :



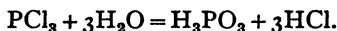
this being practically complete at 300° . When it is volatilised in a space saturated with the vapour of the trichloride, the dissociation of the pentachloride is repressed by mass-action and a density corresponding with PCl_5 was obtained by Wurtz.

Phosphorus pentachloride reacts with some metals, forming the chlorides and phosphorus trichloride :

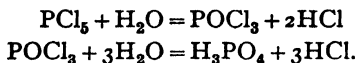


Even gold and platinum react in this way.

Both chlorides of phosphorus are violently and irreversibly hydrolysed by water. The trichloride is completely freed from chlorine, phosphorous acid being formed :



In the case of the pentachloride the reaction proceeds in two stages. With a little water liquid phosphorus oxychloride or phosphoryl chloride POCl_3 is produced (Wurtz, 1847), which is further hydrolysed by excess of water forming orthophosphoric acid H_3PO_4 :



If excess of water is added at once to the pentachloride, phosphoric acid is produced : $\text{PCl}_5 + 4\text{H}_2\text{O} = 5\text{HCl} + \text{H}_3\text{PO}_4$.

Inorganic oxyacids, organic acids (containing the carboxyl group $-\text{CO}\cdot\text{OH}$), and alcohols (hydroxides of hydrocarbon radicals, *e.g.* methyl alcohol $\text{CH}_3\cdot\text{OH}$), containing the hydroxyl group OH , react with phosphorus pentachloride, the hydroxyl group being substituted by an atom of chlorine :



When phosphorus pentachloride is treated with small quantities of water until the solid is completely liquefied, the colourless fuming liquid phosphorus oxychloride or phosphoryl chloride POCl_3 is formed. It is

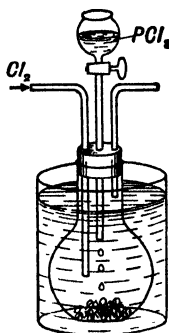


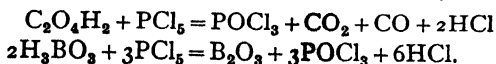
FIG. 219.—Preparation of phosphorus pentachloride.

the chloride of orthophosphoric acid and is also formed by the direct oxidation of phosphorus trichloride by ozone, or by the *gradual* addition of powdered potassium chlorate to phosphorus trichloride and then distilling :



Phosphorus pentachloride and pentoxide combine to form the oxychloride when heated in a sealed tube : $\text{P}_2\text{O}_5 + 3\text{PCl}_5 = 5\text{POCl}_3$.

The action of phosphorus pentachloride on oxalic and boric acids is interesting, since in the first case the by-products are gaseous and are evolved, leaving the phosphorus oxychloride, and in the second case the by-product is non-volatile so that the oxychloride may be distilled off :



The oxychloride is readily hydrolysed by excess of water, forming orthophosphoric acid : $\text{POCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 3\text{HCl}$. With water and excess of zinc dust it gives inflammable phosphine, but PCl_3 does not react in this way.

White phosphorus explodes in contact with liquid chlorine or bromine ; bromine dropped on red phosphorus in a cooled flask reacts with evolution of heat and light and the **tribromide** PBr_3 distils over. By adding bromine to this, the yellow solid **pentabromide** is formed. This dissociates on heating : $\text{PBr}_5 \rightleftharpoons \text{PBr}_3 + \text{Br}_2$. The **oxybromide** POBr_3 is a solid obtained by the action of a small amount of water on the pentabromide, or by distilling PBr_5 with P_2O_5 : $3\text{PBr}_5 + \text{P}_2\text{O}_5 = 5\text{POBr}_3$.

White phosphorus inflames in contact with iodine; if solutions of iodine and phosphorus in carbon disulphide are mixed, the **di-iodide** and **tri-iodide** P_2I_4 and PI_3 are obtained on evaporation. PI_5 and POI_3 are unknown.

OXIDES AND OXYACIDS OF PHOSPHORUS

Three oxides and several oxyacids of phosphorus are known :

—	Hypophosphorous acid, H_3PO_2 .
Phosphorus trioxide, P_2O_3 or P_4O_6 .	Phosphorous acid, H_3PO_3 .
Phosphorus dioxide, P_2O_4 or P_8O_{16} .	Hypophosphoric acid, $\text{H}_4\text{P}_2\text{O}_6$.
Phosphorus pentoxide, P_2O_5 or P_4O_{10} .	Phosphoric acids :
	H_3PO_4 , orthophosphoric acid.
	$\text{H}_4\text{P}_2\text{O}_7$, pyrophosphoric acid.
	HPO_3 , metaphosphoric acid.

The so-called phosphorus sub-oxides, P_4O and P_2O , are impure red phosphorus.

When phosphorus is burnt in a free supply of air phosphorus pentoxide P_2O_5 (first observed by Boyle and called "flowers of phosphorus") is

formed. During the later stages of the combustion in a limited supply of air phosphorus trioxide P_2O_3 is formed. The phosphorus is extinguished before all the oxygen is removed, and a portion is converted into red phosphorus.

Phosphorus trioxide.—The formation of a lower oxide of phosphorus, usually assumed to be P_2O_3 , by the slow oxidation of phosphorus in air (which actually forms mostly P_2O_4) or its combustion in a limited supply of air was noticed by Sage (1777), but the trioxide was first isolated by Thorpe and Tutton in 1890. Phosphorus is burnt in a limited supply of air, and the product condensed by cooling.

Sticks of phosphorus are placed in the hard glass tube *a* (Fig. 220) connected with the Liebig's condenser *b*. A plug of glass wool in this

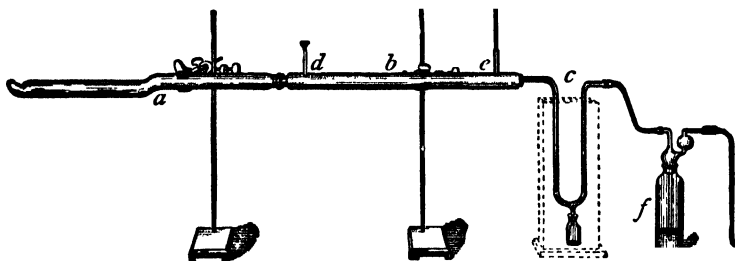
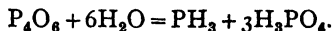


FIG. 220.—Preparation of phosphorus trioxide.

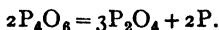
serves to filter out the solid pentoxide formed, whilst the trioxide is kept in the state of vapour by water at 60° in the condenser. The condenser communicates with a U-tube *c*, having a small bottle at the lower part which is immersed in pounded ice and connected through a wash-bottle *f* containing sulphuric acid, with a water-pump for aspirating air through the apparatus. The phosphorus is ignited and a slow current of air drawn through. The reaction is stopped when four-fifths of the phosphorus is burnt. The trioxide condenses in the U-tube; on warming the latter it collects as a liquid in the bottle. This reaction is the only known method of preparing phosphorus trioxide.

Phosphorus trioxide is a white easily fusible crystalline solid. The vapour density corresponds with the formula P_4O_6 . Unless quite pure the trioxide slowly turns red in light owing to the conversion of white phosphorus contained as an impurity into red phosphorus. It is very poisonous and has an unpleasant acid smell. Phosphorus trioxide oxidises in air or oxygen at the ordinary temperature forming the pentoxide, and when gently heated in air or oxygen it inflames. When pure it does *not* glow in air. In chlorine it inflames spontaneously forming $POCl_3$. In cold water phosphorus trioxide dissolves *slowly* (cf. P_2O_5) forming phosphorous acid H_3PO_3 , of which it is the anhydride. Hot water

causes explosive decomposition with formation of phosphine, red phosphorus and phosphoric acid :



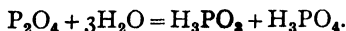
When the liquid trioxide is heated in a sealed tube at 210° it becomes turbid, and at 440° a sublimate of phosphorus dioxide P_2O_4 and a residue of red phosphorus are formed :



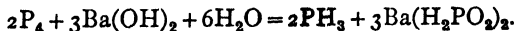
The dioxide is more conveniently obtained by subliming the mixture of oxides obtained by burning phosphorus in a limited supply of dry air :



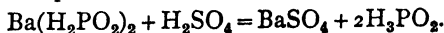
The vapour density of the dioxide corresponds with P_2O_4 . The dioxide with water forms a mixture of phosphorous and phosphoric acids :



Hypophosphorous acid.—The residue from the preparation of phosphine from phosphorus and alkali contains a salt of hypophosphorous acid H_3PO_2 (Dulong, 1816). The barium salt is prepared by heating white phosphorus with baryta water :

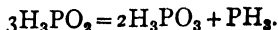


The solution is filtered from barium phosphate, the excess of baryta precipitated by carbon dioxide, the barium hypophosphite $\text{Ba}(\text{H}_2\text{PO}_2)_2$, H_2O recrystallised, and a solution of it decomposed with the calculated amount of dilute sulphuric acid :

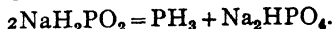


The filtrate is carefully evaporated below 130° to a syrup and cooled in a freezing mixture in a desiccator over P_2O_5 , when it crystallises.

Hypophosphorous acid melts very readily and on heating it decomposes, becoming yellow and evolving phosphine :



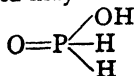
The salts also evolve phosphine on heating :



The acid and its salts are oxidised by permanganate :



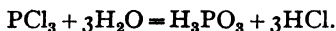
Hypophosphorous acid and its salts are *very powerful reducing agents*, precipitating metals from solutions of their salts. Silver nitrate gives a black precipitate of silver. From copper salts cuprous hydride CuH is precipitated on heating (p. 309). Hypophosphorous acid is *monobasic*, forming crystalline salts such as *sodium hypophosphite* $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and *calcium hypophosphite* $\text{Ca}(\text{H}_2\text{PO}_2)_2$, prepared by heating phosphorus with sodium hydroxide solution and milk of lime, respectively, and used medicinally as tonics. The acid may be formulated as :



which shows that it is monobasic. The hydrogen atoms directly attached to phosphorus have reducing properties (*cf.* phosphorous acid). All hypophosphites are soluble in water. The acid is reduced to phosphine by zinc and hydrochloric acid.

Hypophosphoric acid $\text{H}_4\text{P}_2\text{O}_6$ is formed together with phosphorous acid when white phosphorus slowly oxidises in moist air. The sodium salt is prepared by heating red phosphorus with sodium hypochlorite solution; it forms sparingly soluble crystals $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$. The molecular weight of the ester in solution corresponds with $(\text{C}_2\text{H}_5)_4\text{P}_2\text{O}_6$.

Phosphorous acid.—Phosphorous acid is formed when the trioxide is dissolved in *cold* water but is best prepared by the action of water or concentrated hydrochloric acid on phosphorus trichloride (Davy, 1812):



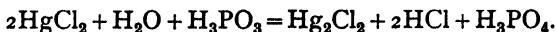
The solution is evaporated until the temperature rises to 180° , hydrogen chloride being driven off, and it then crystallises on cooling. The crystalline acid is also obtained by heating phosphorus trichloride with oxalic acid until frothing ceases, and then cooling:



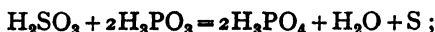
Phosphorous acid forms white fusible crystals very soluble in water. When heated it decomposes evolving phosphine and leaving orthophosphoric acid:



If the acid is heated in air the phosphine ignites and burns in bright flashes. Phosphorous acid is a *powerful reducing agent*, precipitating many metals such as gold from solutions of their salts, and it reduces mercuric to mercurous chloride:

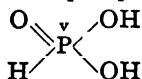


Silver nitrate gives first a white precipitate of silver phosphite, which rapidly turns black from formation of metallic silver: $\text{Ag}_2\text{HPO}_3 + \text{H}_2\text{O} = 2\text{Ag} + \text{H}_3\text{PO}_4$. Phosphorous acid precipitates sulphur from a solution of sulphurous acid:



it is slowly oxidised by solutions of iodine and potassium permanganate.

Wurtz found that phosphorous acid, although it has the formula H_3PO_3 , is *dibasic*; only two atoms of hydrogen can be replaced by metals to form salts. Its preparation from phosphorus trichloride points to the formula $\text{P}(\text{OH})_3$ and normal esters such as triethyl phosphite $\text{P}(\text{OEt})_3$ are known, but the usual dibasic character of the acid is represented by a different formulation with 5-valent phosphorus:



The reducing properties of the acid appear to be due to the hydrogen atom directly attached to phosphorus.

The two series of salts known are MH_2PO_3 and M_2HPO_3 . When boiled with alkalis they do *not* evolve hydrogen (*cf.* hypophosphites). Ordinary sodium phosphite is $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$. An acid sodium salt $2\text{NaH}_2\text{PO}_3 \cdot 5\text{H}_2\text{O}$, a calcium salt $2\text{CaHPO}_3 \cdot 3\text{H}_2\text{O}$ and an acid calcium salt $\text{CaH}_4(\text{PO}_3)_2 \cdot \text{H}_2\text{O}$, are known.

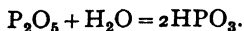
Phosphorus acid reacts with phosphorus pentachloride in the normal manner, forming PCl_3 :



Phosphorus pentoxide.—This oxide is always prepared by the combustion of phosphorus in air or oxygen. On a large scale, the apparatus shown in Fig. 221 is used.

The sheet-iron cylinder is provided with an opening at the side through which a copper spoon containing phosphorus is introduced. The phosphorus is kindled and the pentoxide produced settles out and falls as a voluminous powder into the dry bottle *g*. Commercial phosphorus pentoxide contains some trioxide P_2O_3 and metaphosphoric acid. It may be purified by subliming in a current of dry air or oxygen in a hard glass tube. The purified product should give no black colour with silver nitrate solution.

Phosphorus pentoxide is a white powder which sublimates on heating. The vapour density at 1400° is slightly higher than corresponds with P_4O_{10} . Phosphorus pentoxide has a most powerful affinity for water. The solid rapidly becomes moist and sticky on exposure to air, metaphosphoric acid HPO_3 being formed, and it withdraws the last traces of moisture from gases. These should first be dried by other agents, such as calcium chloride, sulphuric acid or caustic potash, since phosphorus pentoxide soon becomes covered with a skin of metaphosphoric acid which protects the rest from the gas. When thrown into water phosphorus pentoxide reacts with a hissing noise and the evolution of much heat and flocks of metaphosphoric acid are produced :



If the solution is boiled the metaphosphoric acid is converted into a solution of orthophosphoric acid :



This change occurs slowly on standing in the cold, pyrophosphoric acid

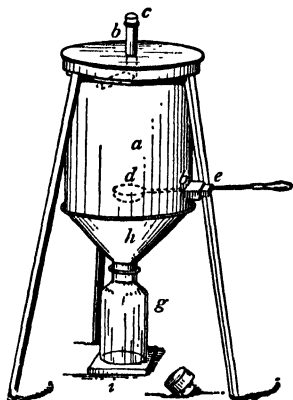


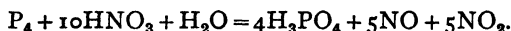
FIG. 221.—Preparation of phosphorus pentoxide.

$\text{H}_4\text{P}_2\text{O}_7$ being formed as an intermediate product. Phosphorus pentoxide withdraws the elements of water from many acids and other substances containing hydrogen and oxygen, forming anhydrides (e.g. SO_3 from H_2SO_4 , N_2O_5 from HNO_3 , Cl_2O_7 from HClO_4).

THE PHOSPHORIC ACIDS

Orthophosphoric acid.—The natural mineral phosphates and bone-ash are salts of orthophosphoric acid H_3PO_4 , and the fertiliser *guano* (excreta of sea birds) is rich in phosphates and also in combined nitrogen. An artificial source of the phosphate used in fertilisers is the *basic slag* of steel furnaces, containing basic calcium phosphate $\text{Ca}_4\text{P}_2\text{O}_9$.

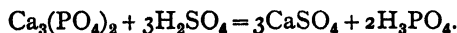
Orthophosphoric acid is formed when phosphorus pentoxide is dissolved in water and the solution boiled. It is prepared in the laboratory by oxidising phosphorus with nitric acid :



The reaction with white phosphorus may be explosive so that red phosphorus is generally used. The details of the experiment are as follows and careful attention to detail is necessary for success.

Place 112 c.c. of concentrated nitric acid and 183 c.c. of water in a 2 litre R.B. flask in the neck of which is a boiling tube through which cold water is circulated to serve as a reflux condenser. Add 31 gm. of red phosphorus in portions of one-fifth at a time to the acid, warming till red vapours appear and cooling if the reaction is too violent. When all the phosphorus is dissolved (neglect any black residue) add 20 c.c. of strong nitric acid and heat in a porcelain dish to oxidise phosphorous acid. When all reaction ceases and a little of the liquid diluted with water gives no black precipitate with AgNO_3 (due to H_3PO_3) add an equal volume of water and filter if necessary. Evaporate in a porcelain dish over a small flame till a thermometer in the liquid rises just to 180° . Cool in a vacuum desiccator over fresh concentrated sulphuric acid, covering the desiccator with a freezing mixture. Deliquescent crystals of orthophosphoric acid are slowly deposited. If the temperature is carried beyond 180° in the evaporation some metaphosphoric acid is formed and crystallisation will not occur.

Orthophosphoric acid is prepared technically by digesting bone-ash or ground phosphate rock with diluted sulphuric acid for several hours :



The calcium sulphate is filtered off and the phosphoric acid evaporated to a syrupy liquid. The product is impure, containing acid calcium phosphate $\text{CaH}_4(\text{PO}_4)_2$. Phosphoric acid is also made by the electric furnace process (p. 499), air being admitted to burn the phosphorus vapour

to P_2O_5 and CO to CO_2 ; water is sprayed into the cooled gas and crude 85 per cent. phosphoric acid is separated by electrostatic precipitation.

Pure orthophosphoric acid is a white deliquescent crystalline solid melting at about 40° , and is very soluble in water. The commercial acid is a concentrated solution, sp. gr. 1.75 (89 per cent. H_3PO_4). The dilute solution has a strong purely acid taste and no smell, and has been used for making "lemonade" as it is not poisonous.

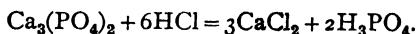
The phosphates.—Orthophosphoric acid is *tribasic* and forms three series of salts, the *orthophosphates*:

Primary, e.g. potassium dihydrogen phosphate KH_2PO_4 .

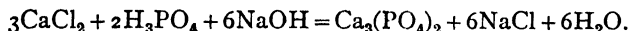
Secondary, e.g. disodium hydrogen phosphate Na_2HPO_4 .

Tertiary, e.g. trisodium phosphate Na_3PO_4 .

Ortho-phosphates are usually called simply "phosphates". The alkali phosphates (except lithium phosphate Li_3PO_4) are soluble in water. The tertiary phosphates of the remaining metals are insoluble in water but dissolve in dilute mineral acids:

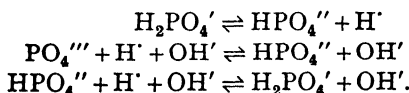


If the acid solutions are neutralised the phosphates are reprecipitated:

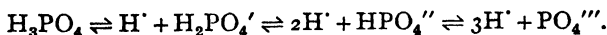


Aluminium and ferric phosphates are insoluble, chromium phosphate is sparingly soluble, and the remaining phosphates are soluble, in acetic acid. These properties are applied in the "phosphate separation" in qualitative analysis.

The soluble primary phosphates in solution are acid to litmus; tertiary phosphates are alkaline; secondary phosphates are faintly alkaline:



The first hydrogen in orthophosphoric acid is easily ionised, the second less easily and the third only in presence of excess of alkali:



On titration with litmus, phosphoric acid behaves as a dibasic acid. Methyl-orange changes colour at the stage NaH_2PO_4 and phenolphthalein practically at the stage Na_2HPO_4 ; the changes occur sharply at 55° . Mixtures of primary potassium and secondary sodium phosphates are used as buffer solutions.*

Orthophosphoric acid and orthophosphates when added to a large excess of ammonium molybdate solution (containing free nitric acid)

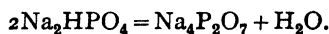
* See Partington and Stratton, *Intermediate Chemical Calculations*, p. 215.

give a canary-yellow precipitate of ammonium phosphomolybdate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$, slowly in the cold (arsenates give no precipitate in the cold) but rapidly on heating. Pyro- and metaphosphates give no precipitate in the cold but on heating they are converted into orthophosphoric acid, which gives a yellow precipitate.

Pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$ is slowly formed (with a little metaphosphoric acid) when orthophosphoric acid is heated at 213° (rapidly above 240°):

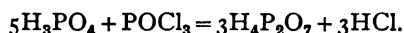


Ordinary sodium phosphate heated above 240° loses water and forms **sodium pyrophosphate** (Clark, 1827):



Whereas the orthophosphate gives a yellow precipitate of silver orthophosphate Ag_3PO_4 with silver nitrate, the residue after heating when dissolved in water gives with silver nitrate a *white* precipitate of silver **pyrophosphate** $\text{Ag}_4\text{P}_2\text{O}_7$.

Pure pyrophosphoric acid is best obtained by gently heating a mixture of crystals of orthophosphoric acid and phosphorus oxychloride:



The product is evaporated *in vacuo* and on cooling in a freezing mixture for some time yields white solid pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$.

A solution of an orthophosphate gives with *magnesia mixture* (a solution containing magnesium chloride, ammonium chloride and ammonia) a white crystalline precipitate of **magnesium ammonium phosphate** $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. In dilute solutions this is deposited slowly but the precipitation is accelerated by adding excess of ammonia and scratching the sides of the beaker with a glass rod, or by shaking violently in a stoppered bottle. When washed with dilute ammonia, dried and heated to dull redness the precipitate loses ammonia and water and forms a white insoluble powder of **magnesium pyrophosphate**:



These reactions are utilised in the detection and estimation of orthophosphoric acid or magnesium. With manganese salts $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Mn}_2\text{P}_2\text{O}_7$ are similarly formed.

If a solution of pyrophosphoric acid is kept for some time or is boiled orthophosphoric acid is formed: $\text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{H}_3\text{PO}_4$. The salts are very stable in solution.

Pyrophosphoric acid contains four hydrogen atoms and is tetrabasic. Only two series of salts are common, viz. the normal salts $\text{M}_4\text{P}_2\text{O}_7$, and the diacid

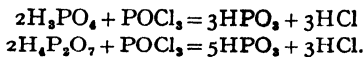
salts $M_2H_2P_2O_7$. Examples are: $Na_4P_2O_7 \cdot 10H_2O$, $Na_2H_2P_2O_7 \cdot 6H_2O$, $Ca_3P_2O_7 \cdot 4H_2O$ (amorphous, insoluble), $Ag_4P_2O_7$ (insoluble), $Ag_2H_2P_2O_7$ (soluble); the salts $NaH_2P_2O_7$ and $Na_2HP_2O_7$ are known.

Metaphosphoric acid is formed when either ortho- or pyro-phosphoric acid is heated at 316° (best in a gold crucible): $H_3PO_4 = HPO_3 + H_2O$ (Graham, 1833). It is a sticky mass. By prolonged heating to redness some phosphoric anhydride appears to be produced and the hard glass formed on cooling crackles when thrown into water. The water content of the residue depends on the duration of heating; pyrophosphoric acid is formed as an intermediate product. At a white heat the acid volatilises and the vapour density corresponds with the formula $(HPO_3)_2$.

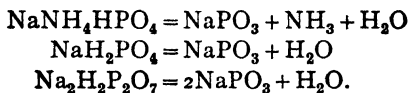
Metaphosphoric acid is also formed on heating ammonium phosphate:



Pure metaphosphoric acid is best obtained by gently heating the solid ortho- or pyro-acid and phosphorus oxychloride:



Sodium metaphosphate is formed as a clear glass when microcosmic salt, acid sodium orthophosphate, or acid sodium pyrophosphate is heated to redness:



If a little microcosmic salt is heated on a loop of platinum wire a fused bead of $NaPO_3$ remains, which dissolves many metallic oxides with the formation of orthophosphates possessing characteristic colours ("microcosmic bead"): $CoO + NaPO_3 = CoNaPO_4$ (blue).

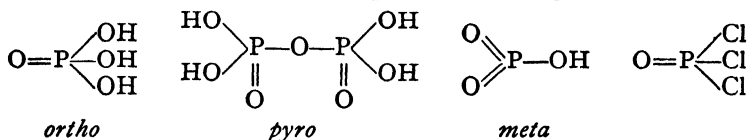
A solution of a metaphosphate gives a white gelatinous precipitate of **silver metaphosphate** $AgPO_3$ with silver nitrate.

Metaphosphoric acid, unlike the other phosphoric acids, at once coagulates albumin (white of egg), and gives a white precipitate with barium chloride in acid solution.

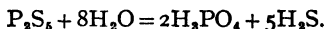
Sodium tripolyphosphate, $Na_5P_3O_{10}$, made by heating a mixture of mono- and disodium phosphates, is largely used in detergents: $NaH_2PO_4 + 2Na_2HPO_4 = Na_5P_3O_{10} + 2H_2O$. **Sodium polymetaphosphate** or *Graham's salt*, previously regarded as hexametaphosphate but more highly polymerised, $(NaPO_3)_n$, is formed as a glass on fusing the monophosphate, acid pyrophosphate, or microcosmic salt and rapid cooling. It forms complexes with calcium ions which give no precipitate with soap so that the salt is used in laundries for softening water. No scale is deposited in steam

boilers when this salt has been added to hard water, and scale already formed is dissolved.

The structural formulae of the phosphoric acids and phosphorus oxychloride may be written as follows, phosphorus being 5-valent :



Phosphorus sulphides.—Several sulphides of phosphorus are formed by heating red phosphorus and sulphur in the correct proportions. The most important are **tetraphosphorus trisulphide** (commonly called "sesquisulphide") P_4S_3 , used in the manufacture of matches (p. 504), and **phosphorus pentasulphide** P_2S_5 . The pentasulphide is hydrolysed by water with evolution of hydrogen sulphide :



The atomic weight of phosphorus has been determined from the ratios $\text{PCl}_3 : 3\text{AgCl}$, $\text{PBr}_3 : 3\text{AgBr}$, and $\text{Ag}_3\text{PO}_4 : 3\text{AgBr}$. An accurate value has also been found by Ter-Gazarian from the limiting density of pure phosphine (PH_3). The valency is found from the densities of PH_3 and PCl_3 and from the atomic heat of white phosphorus.

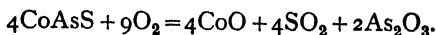
ARSENIC

History.—The native sulphides of arsenic *realgar* As_2S_3 and *orpiment* As_2S_3 were known in very early times; they occur in old Egyptian and Hittite remains and were used as pigments. In Classical times orpiment was called *arsenikon* and *auripigmentum*, and the alchemists obtained arsenious oxide As_2O_3 by roasting the sulphides in air and used it for whitening copper, with which arsenic forms a white alloy. That "white arsenic" (As_2O_3) was the "calx" (oxide) of a semi-metal was recognised by Brandt in 1733.

Occurrence.—Elementary arsenic is found native. The chief minerals are the sulphides *orpiment* (As_2S_3) and *realgar* (As_2S_2); the oxide *arsenolite* As_2O_3 ; *arsenical iron* FeAs_2 ; *arsenical nickel* NiAs ; *nickel glance* NiAsS ; *arsenical pyrites* or *mispickel* FeAsS or Fe_2AsS_2 ; *cobaltite* CoAsS ; and some salts of arsenic acid H_3AsO_4 , e.g. *cobalt bloom* $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$.

Iron pyrites and other sulphide ores often contain arsenic and sulphuric acid prepared from arsenical pyrites may contain arsenious oxide As_2O_3 . Coal smoke, especially in yellow fogs, may contain arsenious oxide from pyrites in the coal. *Traces* of arsenic occur in some mineral waters, in the human body, and in most foods.

Preparation.—In roasting minerals in a current of air for metallurgical treatment, fumes of impure arsenious oxide As_2O_3 are often evolved and may be condensed in flues as a powder :



This may be obtained in larger quantities by roasting rich arsenical ores such as mispickel in a current of air in a revolving calciner (Fig. 222),

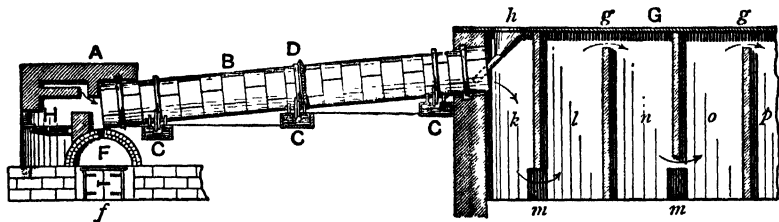
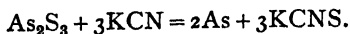


FIG. 222.—Oxland and Hocking's revolving calciner.

a rotating iron cylinder lined with refractory material down which the crushed ore slides and is met by flames and hot gases from a furnace at the lower end. The "arsenical soot" is collected in flues, and the roasted ore freed from arsenic drops into a wagon for use in the smelting furnace.

The arsenious oxide is purified by sublimation in iron pots, and the *white arsenic* obtained is the source of all the arsenic compounds of commerce. Arsenious oxide is used as a poison for vermin, for weed-killer, in taxidermy for preserving skins, in glass-making for removing colour from the glass, and in minute amounts medicinally as a tonic and in skin and other diseases. *All compounds of arsenic are very poisonous and care must be exercised in all experiments with them.*

The element arsenic is obtained by heating arsenical pyrites with iron or by reducing arsenic trioxide with charcoal. The powdered mixture is heated in a clay crucible covered with an inverted iron cone into which the arsenic sublimes: $\text{As}_2\text{O}_3 + 3\text{C} = 2\text{As} + 3\text{CO}$. It is also prepared by heating mispickel in a clay tube fitted for half its length with an inner tube of sheet iron. The iron tube is afterwards unrolled to split off the arsenic, which is purified by resublimation from charcoal powder: $\text{FeAsS} = \text{FeS} + \text{As}$. Arsenic sulphides are *not* reduced by heating with charcoal but are reduced by potassium cyanide :



As in the case of phosphorus, the element arsenic exists in different allotropic forms :

(1) **Yellow arsenic** corresponding with white phosphorus; soluble in carbon disulphide; an unstable form; sp. gr. 2.026.

(2) **Black arsenic** formed together with grey arsenic when arsenic vapour is slowly cooled ; sp. gr. 4.7 ; insoluble in carbon disulphide.

(3) **Grey arsenic** (" metallic arsenic ") the stable and ordinary form corresponding with " metallic " phosphorus ; sp. gr. 5.73 ; insoluble in carbon disulphide.

Yellow arsenic is obtained by subliming ordinary arsenic in a current of carbon dioxide and suddenly cooling the gas. It forms yellow crystals which oxidise with phosphorescence in air, an odour of garlic being emitted. On exposure to light it forms grey arsenic.

Grey arsenic forms steel-grey brittle crystals with a metallic lustre and is a fairly good conductor of heat and electricity. On heating it sublimes without previous fusion forming a colourless vapour, the density of which at 860° corresponds with As_4 . At higher temperatures dissociation into As_2 occurs. When heated in a sealed tube arsenic melts under pressure at 814°.

Grey arsenic is not oxidised in dry air but in presence of moisture it rapidly becomes covered with a blackish-grey film containing the trioxide. When heated in air it phosphoresces and then burns with a white flame. It burns brilliantly in oxygen forming the trioxide : $\text{As}_4 + 3\text{O}_2 = 2\text{As}_2\text{O}_3$.

1 gm. of arsenic is heated in a current of oxygen in a hard glass tube connected with an empty flask, the exit tube from which passes to a U-tube packed with glass wool to keep back arsenious oxide. The arsenic burns with a brilliant flame, producing white solid arsenious oxide.

Powdered arsenic takes fire in chlorine forming the trichloride, and burns in contact with liquid bromine forming the tribromide. Arsenic combines with most metals to form fusible arsenides and when alloyed with lead it makes the latter harder and more fusible. If this alloy is allowed to flow through a sieve, the drops of fused metal falling down a tower into water assume a spherical shape and form shot.

Hydrochloric acid dissolves arsenic only in the presence of air, when the trioxide is probably first formed. Dilute nitric acid has little action in the cold ; on heating it slowly oxidises arsenic to arsenious oxide and concentrated nitric acid or *aqua regia* rapidly oxidises it to arsenic acid H_3AsO_4 (and with *aqua regia* some trichloride AsCl_3). Hot concentrated sulphuric acid is reduced to sulphur dioxide :



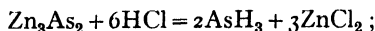
Arsenic is insoluble in aqueous alkalis but is attacked by fused alkalis forming arsenites and hydrogen : $2\text{As} + 6\text{NaOH} = 2\text{Na}_3\text{AsO}_3 + 3\text{H}_2$.

Arsenic hydride.—The only hydrogen compound of arsenic definitely known is AsH_3 , also called *arsine* or *arseniuretted hydrogen*, a colourless

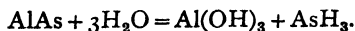
gas. It is not formed by direct combination of the elements. It was formerly supposed to be formed by the growth of moulds in contact with wallpaper coloured with Scheele's green (copper arsenite) but the gaseous arsenical compound so formed is said to be trimethyl arsine $(\text{CH}_3)_3\text{As}$.

Arsine is formed by the action of *nascent* hydrogen on a soluble arsenic compound. When a solution of arsenious oxide is added to a mixture of zinc and dilute sulphuric acid evolving hydrogen, or to sodium amalgam, the gas acquires a very unpleasant smell of garlic and burns with a lilac flame. Scheele first obtained arsine in 1775 by the action of arsenic acid on zinc. It is formed at the cathode by the electrolysis of solutions of arsenious oxide, and by boiling a soluble arsenic compound with zinc and caustic potash; antimony does *not* form a hydride in the latter reaction (*Fleitzmann's test*). The gas obtained by all these processes is largely diluted with hydrogen. If it is passed through a tube cooled in liquid air the arsine is liquefied and the pure gas is evolved on warming.

Pure arsine (*which is dangerously poisonous*) may be prepared by the action of dilute hydrochloric acid on zinc arsenide Zn_3As_2 (obtained by heating together arsenic and zinc in a closed crucible):



or by the action of warm water on aluminium arsenide (obtained by heating together aluminium powder and powdered arsenic in a covered crucible):



On exposure to light in the moist condition arsine is rapidly decomposed with deposition of arsenic. When quite pure and dry the gas is stable. Arsine is decomposed by heat (it begins to decompose at 230°) into its elements: $2\text{AsH}_3 = 2\text{As} + 3\text{H}_2$. From the ratio of the volumes of arsine and hydrogen, and the density, the formula of the gas is found as in the case of phosphine (p. 506).

Arsine differs from ammonia and resembles phosphine in being readily combustible and almost insoluble in water and ether. It is almost insoluble in alcohol, but dissolves readily in turpentine. It is neutral and does *not* combine with acids to form salts analogous to ammonium and phosphonium salts.

Tests for arsenic.—The formation of arsine and its decomposition by heat are applied in the very delicate **Marsh-Berzelius test**.

Hydrogen generated from pure zinc and pure dilute sulphuric acid is freed from traces of hydrogen sulphide by a roll of dry lead acetate paper in the first part of the drying tube, the second half of which is packed

with calcium chloride (Fig. 223). The dry gas passes through a hard glass tube constricted as shown and heated at one point by a small bunsen flame. If the materials are free from arsenic, no stain is produced in the tube. If a *dilute* solution of arsenious oxide or any material to be tested

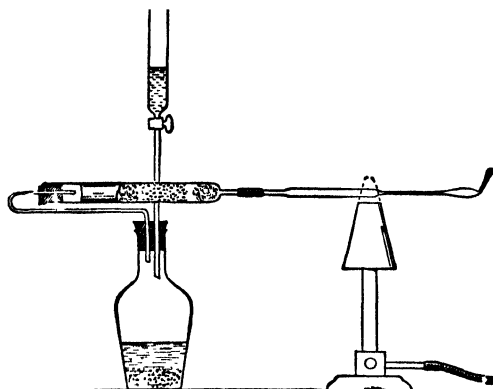


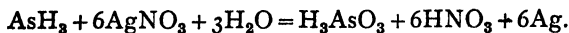
FIG. 223.—Marsh-Berzelius arsenic test.

for arsenic is added to the flask, arsine is formed and is decomposed in the hot tube, a brown or black mirror being deposited beyond the heated portion. After a sufficient time, the whole of the arsenic is expelled from the solution as arsine, and by comparing the mirror with standard tubes prepared with known small amounts of arsenious oxide a quantitative estimation may be made. Some

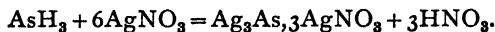
varieties of zinc do not easily reduce arsenic compounds but they may be rendered active by adding a little soluble cadmium salt to the solution in the flask. A type of apparatus in which the hydrogen is generated electrolytically is also used; in this case arsenates are also reduced if a mercury cathode is used.

If the tube is not heated but the gas kindled at the jet, the lilac flame deposits black spots of arsenic on the outer surface of a glazed porcelain dish filled with water: these are produced by decomposition by heat: $2\text{AsH}_3 = 2\text{As} + 3\text{H}_2$; they dissolve readily in a solution of sodium hypochlorite or bleaching powder forming arsenates, *e.g.* Na_3AsO_4 , but are insoluble in tartaric acid. If a spot is moistened with yellow ammonium sulphide and this evaporated by gentle heating, a *bright yellow* spot of arsenic trisulphide As_2S_3 is left (*cf.* antimony hydride).

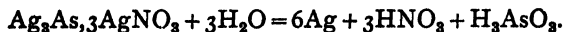
Arsine passed into dilute silver nitrate solution gives a black precipitate of metallic silver and the filtrate contains arsenious acid (*cf.* antimony):



With concentrated silver nitrate solution no precipitate is formed but a yellow solution of a double compound of silver arsenide and nitrate:



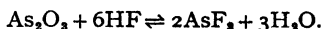
On dilution with water a black precipitate of silver is deposited:



If the gas is passed into mercuric chloride solution a yellow coloration is produced; on further treatment this becomes brown and finally black. This is the basis of the sensitive *Gutzeit test*.

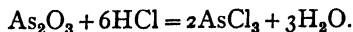
The solution is added to pure zinc and arsenic-free dilute hydrochloric acid in a small bottle, a little stannous chloride being added to reduce any 5-valent arsenic. The bottle is fitted with a vertical tube holding a roll of lead acetate paper, at the top of which is a rubber stopper. A piece of filter paper previously moistened with mercuric chloride solution and dried is placed over the hole of the stopper and another stopper placed on the top, the two being kept together with a spring clip. The yellow stain on the paper is compared with standards. The yellow substance may be $\text{AsH}(\text{HgCl})_2$.

Halogen compounds of arsenic.—Arsenic combines directly with all the halogen elements. Arsenic trifluoride AsF_3 , a colourless fuming liquid, is prepared by heating a mixture of arsenious oxide, powdered fluorspar and concentrated sulphuric acid in a lead retort:

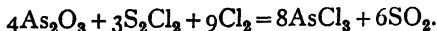


The water produced in the reaction is retained by the sulphuric acid, otherwise hydrolysis of the fluoride would occur. Arsenic pentafluoride AsF_5 is a colourless gas, formed by the reaction $\text{AsF}_3 + 2\text{SbF}_5 + \text{Br}_2 = \text{AsF}_5 + 2\text{SbBrF}_4$, but the pentachloride does not seem to exist.

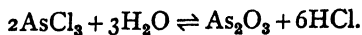
Arsenic trichloride AsCl_3 was discovered by Glauber in 1648 and is the most important halogen compound of arsenic. It is formed when arsenic burns in chlorine gas—a reaction which occurs spontaneously even if the materials are very carefully dried—by heating arsenic with mercuric chloride, by heating arsenious oxide in chlorine, or by distilling a mixture of arsenious oxide, common salt and concentrated sulphuric acid in a retort and condensing the vapour in a cooled receiver. The distillate is freed from excess of chlorine by distillation over powdered arsenic:



The most convenient method of preparation is to heat arsenious oxide with sulphur chloride under a reflux condenser, pass chlorine through the mixture, and distil:

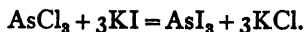


Arsenic chloride is a colourless fuming liquid, b.pt. 130° , which forms pearly crystals in a freezing mixture. It is hydrolysed by water:



The hydrolysis is reversible, showing that arsenic has some metallic properties; if arsenious oxide is dissolved in fairly concentrated hydrochloric acid and the liquid boiled, arsenious chloride distils over with the steam.

Arsenic tribromide AsBr_3 and arsenic tri-iodide AsI_3 are white and red solids, respectively, formed from the elements; the tri-iodide, which is only slightly hydrolysed by water, is also precipitated on adding a solution of arsenious oxide in hydrochloric acid to a solution of potassium iodide:



ARSENIC OXIDES

Oxides and oxyacids of arsenic.—Arsenic forms two oxides, As_2O_3 and As_2O_5 . Arsenious oxide forms salts called arsenites and arsenic pentoxide forms arsenic acid H_3AsO_4 and arsenates.

Arsenious oxide, the most important compound of arsenic (known in commerce as "white arsenic", or simply as "arsenic") exists in three modifications: (1) an amorphous glass, (2) octahedral crystals (the common form), and (3) monoclinic crystals (found native as *claudetite*). The vapour density corresponds with the formula As_4O_6 , but at higher temperatures dissociation into As_2O_3 occurs.

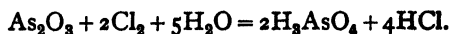
The amorphous variety is formed when the vapour is slowly condensed at a temperature slightly below the point of vaporisation. It may be kept in sealed tubes but in presence of moisture it becomes opaque and slowly passes into the octahedral form. If the glass is dissolved in hydrochloric acid and the solution allowed to cool, crystals are deposited, each accompanied by a flash of light.

The octahedral form is stable under ordinary conditions and is produced when the vapour is *rapidly* condensed, when the trioxide is crystallised from water or hydrochloric acid, or spontaneously with evolution of heat from the vitreous form. It sublimes on heating without melting but can be fused under pressure.

The monoclinic variety is formed by crystallisation from a boiling saturated solution of the amorphous substance in potassium hydroxide solution or by sublimation under special conditions.

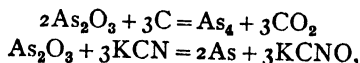
If arsenious oxide is heated in a sealed tube at 400° the vitreous form remains at the bottom of the tube, the monoclinic form sublimes to the intermediate part at 200° , and the octahedral form sublimes to the top of the tube. The different crystalline forms may be recognised with a good lens.

Arsenious oxide is easily *oxidised* to arsenic pentoxide As_2O_5 , arsenic acid H_3AsO_4 or an arsenate, by means of ozone, hydrogen peroxide, chlorine, *aqua regia*, bromine, iodine, nitric acid, and hypochlorites (especially in alkaline solution):

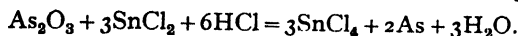


It precipitates red cuprous oxide from Fehling's solution.

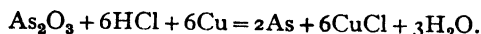
Arsenious oxide is easily *reduced* to arsenic by heating with charcoal or potassium cyanide, when a mirror of arsenic sublimes :



or by a solution of stannous chloride which gives a brown precipitate :



If arsenious oxide is boiled with hydrochloric acid and copper foil, a grey deposit of arsenic forms on the copper :



If the copper foil is washed, dried and heated in a tube, a crystalline sublimate of arsenious oxide is formed (*Reinsch's test*). The mere change of colour of the copper is not decisive.

Arsenious oxide is a violent poison : 0.06 gm. is a dangerous dose and 0.125–0.25 gm. is fatal. Habitual use of small quantities renders the system immune to much larger doses, and the peasants of Styria are said to be able to consume arsenious oxide in amounts (0.3 gm.) which would ordinarily be fatal.* Freshly precipitated ferric hydroxide obtained by adding magnesia to a solution of ferric chloride adsorbs arsenious oxide, and is recommended as an antidote in cases of poisoning. Certain moulds seem to thrive on arsenic compounds (p. 523).

Arsenious oxide is only sparingly soluble in water (about 1 per cent. at 15°); the solution has a feebly acid reaction and appears to contain arsenious acid H_3AsO_3 , although this is not known in the solid state. It is a very weak acid.

The finely powdered oxide is not easily wetted by water but a solution can be prepared by boiling. It dissolves in warm sodium bicarbonate solution with evolution of carbon dioxide and formation of sodium arsenite Na_3AsO_3 or NaAsO_2 . This solution is often used for the standardisation of iodine solution, which oxidises arsenite to arsenate :

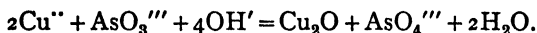


The excess of bicarbonate has no action on the iodine, whilst if the arsenious oxide were dissolved in alkali hydroxide the latter would react with iodine.

The *arsenites* (which are not well defined) correspond with the *hypothetical* arsenious acids : *ortho*- (H_3AsO_3), *pyro*- ($\text{H}_4\text{As}_2\text{O}_5$) and *meta*-

* According to Brande (*Manual of Chemistry*, 1848, vol. i, p. 915) the taste of arsenious oxide "is sometimes described as insipid, and some have represented it as acrid and acid. When the tongue is applied to the vitreous acid, it at first seems nearly tasteless, afterwards slightly acid, sweet and astringent". The student is recommended to abstain from the experiment. The same authority (p. 918) states that arsenic pentoxide (which is much more soluble) "tastes acid and metallic, and is a virulent poison".

(HAsO_2). **Sodium arsenite** Na_3AsO_3 is an amorphous powder soluble in and hydrolysed by water and is obtained by dissolving arsenious oxide in sodium hydroxide solution and evaporating to dryness. A solution is used as a weed-killer. A solution of an arsenite gives with silver nitrate a yellow precipitate of **silver arsenite** Ag_3AsO_3 , soluble in acetic acid (the yellow silver phosphate Ag_3PO_4 is insoluble). Copper sulphate gives a bright green precipitate of **Scheele's green**, used as an insecticide. This may be CuHAsO_3 or $\text{Cu}_3(\text{AsO}_3)_2 \cdot 2\text{H}_2\text{O}$, *i.e.* cupric arsenite. When dissolved in alkali and boiled, an arsenate is formed and cuprous oxide precipitated :



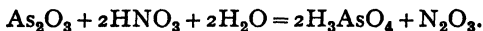
The brilliant pigment **Schweinfurt green** or **Paris green**, used as an insecticide, has the composition $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$, and is obtained by boiling verdigris (a basic acetate of copper) with arsenious oxide and acetic acid.

Arsenic pentoxide and arsenic acid.—Arsenic on burning in oxygen yields the trioxide (*cf.* phosphorus). The **pentoxide** As_2O_5 is obtained by heating arsenic acid at 200° :



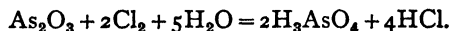
It is a deliquescent white solid which melts at a red heat and evolves oxygen : $\text{As}_2\text{O}_5 = \text{As}_2\text{O}_3 + \text{O}_2$.

Arsenic acid H_3AsO_4 was discovered by Cavendish in 1764 and by Scheele in 1775, and is obtained by boiling arsenious oxide with concentrated nitric acid (see p. 492) :

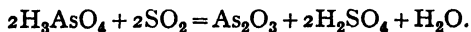


The very concentrated solution on cooling deposits rhombic crystals of **orthoarsenic acid** $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ (sometimes H_3AsO_4 separates). **Pyroarsenic acid** $\text{H}_4\text{P}_2\text{O}_7$ is obtained in crystals by evaporating a solution of arsenic acid in an open dish until the temperature rises to 170° to 180° , and cooling. Meta-arsenic acid is apparently not known, although it has been said to be formed at 200° .

Arsenic acid is also produced by heating arsenious oxide with *aqua regia* or passing chlorine through a suspension of arsenious oxide in water:



Arsenic acid in solution is reduced by sulphur dioxide to arsenious oxide :

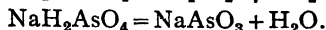
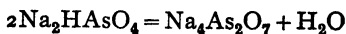


It liberates iodine from potassium iodide and hydrochloric acid and is an oxidising agent :

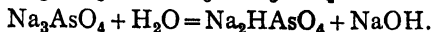
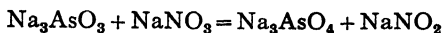


The **arsenates** are isomorphous with the phosphates and probably have similar constitutional formulae. The normal ortho-arsenates exist as

solids and in solution, but the pyro- and meta-arsenates exist only as solids and are prepared by heating the acid and di-acid ortho-salts, as in the case of phosphates :



The salt $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ is largely used in calico-printing. It is made by fusing sodium arsenite with sodium nitrate, and crystallising :

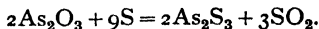


The pure salt is made from arsenic acid solution and sodium carbonate and evaporating. Lead arsenate $\text{Pb}_3(\text{AsO}_4)_2$ is used in spraying fruit trees to kill caterpillars.

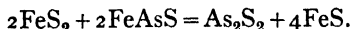
Ammonium molybdate and concentrated nitric acid give with arsenates a yellow precipitate similar to that obtained with phosphates *but only on heating*. Magnesia mixture gives a white crystalline precipitate of **magnesium ammonium arsenate** $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, similar to $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. On heating this leaves a residue of **magnesium pyro-arsenate** $\text{Mg}_2\text{As}_2\text{O}_7$.

The precipitate of magnesium ammonium arsenate is distinguished from the phosphate as follows. It is dissolved in dilute hydrochloric acid and the hot solution reduced to arsenious oxide with sulphur dioxide. The excess of sulphur dioxide is removed by boiling and hydrogen sulphide passed in. Yellow arsenious sulphide is precipitated. The filtrate is boiled to remove H_2S and gives a precipitate of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ when made alkaline with ammonia if a phosphate is also present. Arsenates are also distinguished from phosphates by giving with silver nitrate in neutral solution a *light chocolate-brown* precipitate of **silver arsenate** Ag_3AsO_4 , soluble in dilute nitric acid and in ammonia. Phosphates give a *yellow* precipitate of Ag_3PO_4 . If an arsenite is present it may be detected by dissolving the precipitate in dilute nitric acid, avoiding excess, and adding ammonia drop by drop. Brown silver arsenate is first precipitated, then yellow silver arsenite.

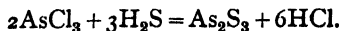
Arsenic sulphides occur native as *realgar* As_2S_2 and *orpiment* As_2S_3 . Orpiment may be prepared by heating a mixture of arsenious oxide and sulphur in the correct proportions :



Realgar is made by distilling iron pyrites with arsenical pyrites :



The trisulphide is easily prepared by passing hydrogen sulphide into a solution (containing AsCl_3) of arsenic trioxide in dilute hydrochloric acid :

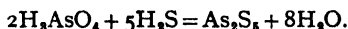


If hydrogen sulphide is passed into a solution of arsenious oxide in distilled water no precipitate is formed but a yellow colloidal solution of arsenic trisulphide. Arsenic sulphide is precipitated from this by dilute hydrochloric acid or salts.

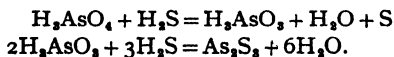
Realgar is used in pyrotechny. *Bengal fire* is a mixture of nitre, sulphur and realgar. Mixed with slaked lime realgar is used as a depilatory in tanning to remove hair from hides; a mixture of orpiment and slaked lime is also used for removing superfluous hair. In both cases the active agent is probably calcium hydrosulphide $\text{Ca}(\text{SH})_2$, which dissolves hair. A mixture of orpiment with arsenic trioxide, obtained by subliming the latter with sulphur, is the pigment *King's yellow*.

Both sulphides of arsenic burn when heated in air forming sulphur dioxide and volatile arsenic trioxide. They are oxidised by nitric acid but are insoluble in hot concentrated hydrochloric acid (Sb_2S_3 is soluble).

Arsenic pentasulphide As_2S_5 is precipitated when hydrogen sulphide is passed rapidly into a warm solution of arsenic acid containing hydrochloric acid :



If the reaction takes place slowly and in the cold, a white precipitate of sulphur is first formed and the arsenic acid is reduced to arsenious acid. The arsenious acid is precipitated as arsenious sulphide :



The reaction is quicker in hot solutions. In qualitative analysis solutions of arsenates are first reduced with sulphurous acid before treating with hydrogen sulphide.

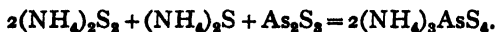
Arsenic trisulphide dissolves readily in alkali hydroxide or ammonia solutions, and even in a warm solution of ammonium carbonate (antimony trisulphide is insoluble). The product is a mixture of an arsenite and a thioarsenite : $\text{As}_2\text{S}_3 + 6\text{KOH} = \text{K}_3\text{AsO}_3 + \text{K}_3\text{AsS}_3 + 3\text{H}_2\text{O}$.

If an acid is added, the whole of the arsenic is precipitated as arsenious sulphide : $\text{K}_3\text{AsO}_3 + \text{K}_3\text{AsS}_3 + 6\text{HCl} = 6\text{KCl} + 3\text{H}_2\text{O} + \text{As}_2\text{S}_3$.

If arsenic trisulphide is dissolved in an alkali sulphide a thioarsenite alone is formed : $3\text{K}_2\text{S} + \text{As}_2\text{S}_3 = 2\text{K}_3\text{AsS}_3$.

The thioarsenites are sometimes formulated as meta-salts (KAsS_2), as are the arsenites (KAsO_2).

By dissolving arsenic trisulphide in solutions of alkali polysulphides (*e.g.* yellow ammonium sulphide) thioarsenates are formed :



On acidifying, a yellow precipitate of a mixture of arsenic trisulphide and sulphur is formed and hydrogen sulphide is evolved :



The atomic weight of arsenic is determined from the ratios $\text{Ag}_3\text{AsO}_4 : 3\text{AgCl}$ and $\text{Ag}_3\text{AsO}_4 : 3\text{AgBr}$. The valency is found from the atomic heat, the vapour density of volatile compounds, *e.g.* AsCl_3 , and the isomorphism of phosphates and arsenates.

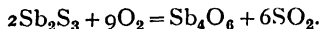
ANTIMONY

History.—Native black antimony sulphide was used very sparingly as an eye paint in ancient Egypt and (with the commoner galena) was called *mestem*, which became the Greek *stimmi*. Metallic antimony was also known, *e.g.* an ancient Chaldaean vase of 3000 B.C. is of pure antimony. The Latin name *stibium* (our *stibnite*), derived from the Greek, usually denoted the sulphide although Pliny says a "lead" can be obtained from it. The compounds of antimony are rather fully described in the apocryphal *Triumphal Chariot of Antimony* of "Basil Valentine", which was probably compiled by its "editor" Thoele about 1600.

Occurrence.—Antimony occurs in small amounts in the metallic state and as the oxide Sb_2O_3 in the mineral *valentinite*. The principal ore is antimony sulphide Sb_2S_3 (*stibnite*) which occurs in China, France and Italy in the form of black or grey crystals (often radiating needles) or as compact masses.

Metallurgy.—In the preparation of antimony stibnite is first *liquated*, *i.e.* heated so that the readily fusible sulphide of antimony flows away from the rock. The sulphide is then reduced by heating with iron and a little salt in plumbago crucibles : $\text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeS}$. The metal (*regulus of antimony*) melts and collects below the slag.

The sulphide may also be carefully roasted in a reverberatory furnace, when antimony dioxide Sb_2O_3 is left. At higher temperatures the trioxide Sb_4O_6 sublimes :



The antimony oxides are mixed with charcoal and sodium carbonate and heated to redness, when reduction occurs : $\text{Sb}_2\text{O}_3 + 3\text{C} = 2\text{Sb} + 3\text{CO}$. The regulus is purified by fusing with sodium carbonate and a little nitre. It then crystallises on cooling in beautiful star-shaped or fern-like forms on the surface.

Properties.—Antimony is a silver-white lustrous brittle metal which is easily powdered. It melts fairly easily (630°) but (unlike phosphorus and arsenic) it boils only at a very high temperature. The vapour density points to the presence of Sb_4 and Sb_2 molecules in the vapour.

Antimony is rather a poor conductor of heat and electricity. The metal is precipitated as a fine black powder by zinc from a solution of antimony trichloride; this powder is used for covering plaster casts to give them the appearance of steel.

When a piece of zinc is laid on a piece of platinum foil in an acidified solution of an antimony salt a black stain of antimony is deposited on the platinum. If a tin salt is present metallic tin is deposited on the zinc.

Antimony is unchanged in air and is not acted upon by water or dilute acids. It decomposes steam at a red heat and is oxidised by concentrated nitric acid, giving oxides of nitrogen and a white powder of hydrated antimony pentoxide. The *pure* metal does not dissolve in concentrated hydrochloric acid in absence of oxygen, but the commercial metal dissolves on heating. Antimony is attacked by hot concentrated sulphuric acid forming the sulphate $\text{Sb}_2(\text{SO}_4)_3$, and dissolves readily in *aqua regia* forming a solution of the pentachloride SbCl_5 .

When strongly heated in air antimony burns, evolving white fumes of the trioxide Sb_2O_3 . A bead of antimony when heated on charcoal before the blowpipe continues to burn when the flame is removed, and if dropped on a piece of paper turned up at the edges the bead breaks up into burning globules, which disperse and leave curious charred tracks on the paper. Antimony burns brilliantly in oxygen, even in complete absence of moisture. It also ignites spontaneously in chlorine.

Unstable allotropic forms of antimony are known. **Yellow antimony** is amorphous and soluble in carbon disulphide and is formed by the action of ozonised oxygen or chlorine on liquid stibine. Another form is **explosive antimony**, obtained by Gore in 1854 by the slow electrolysis of a solution of antimony trichloride in hydrochloric acid with a cathode of platinum wire and an antimony anode. The metal deposited on the cathode resembles polished graphite and when scratched it is explosively converted into ordinary antimony with evolution of heat and fumes of SbCl_3 , which it always contains.

Antimony is a constituent of several important alloys. A mixture of antimony and lead is *hard lead* or *antimonial lead*, used for stopcocks for sulphuric acid. The most important alloys of the metal are those with lead and tin used for *type metal*. These expand on solidification. *Pewter* and *Britannia metal* are alloys of tin, antimony, and a little copper. With copper antimony forms a beautiful purple alloy called *regulus of Venus* with the composition Cu_2Sb .

Antimony hydride.—Antimony and hydrogen do not combine directly but the hydride SbH_3 or *stibine* is formed mixed with hydrogen when a solution of an antimony salt is added to zinc and dilute sulphuric acid,

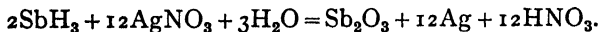
when reduction by nascent hydrogen occurs (L. Thompson, 1837). The gas burns with a grey flame producing fumes of the trioxide. A black stain of antimony is deposited on a cold porcelain dish held in the flame and on both sides of the heated spot on passing the gas through a heated glass tube (arsenic is deposited from arsine only on the side furthest from the generating flask) : $2\text{SbH}_3 = 2\text{Sb} + 3\text{H}_2$.

To distinguish the product from the similar but brighter arsenic mirror, three spots are formed on the dish, which are treated as follows :

<p>(1) Moisten with a solution of bleaching powder : As dissolves : $5\text{Ca}(\text{OCl})_2 + 6\text{H}_2\text{O} + \text{As}_4 = 5\text{CaCl}_2 + 4\text{H}_2\text{AsO}_4$. Sb is insoluble.</p>	<p>(2) Moisten with a concentrated solution of tartaric acid : As is insoluble. Sb dissolves forming $(\text{SbO})_2\text{C}_4\text{H}_4\text{O}_6$.</p>	<p>(3) Moisten with yellow ammonium sulphide and evaporate : As gives a yellow residue of As_2S_3. Sb gives an orange residue of Sb_2S_3.</p>
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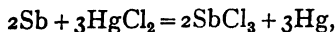
A purer gas is obtained by the action of dilute sulphuric acid on an alloy of zinc or magnesium and antimony. The pure gas may be collected over mercury and is fairly stable when dry. It has an unpleasant odour and is poisonous. It is attacked by air or oxygen forming water and antimony, and decomposes into its elements in presence of moisture or with explosion when heated or sparked or sometimes spontaneously, as it is strongly endothermic. The density corresponds approximately with the formula SbH_3 .

When hydrogen containing stibine is passed into a solution of silver nitrate a black precipitate is formed and the filtrate contains no antimony, whereas if arsenic hydride is present the filtrate contains the whole of the arsenic. The precipitate first formed is silver antimonide SbAg_3 , but this is rapidly decomposed by the excess of silver nitrate, forming a black mixture of silver, antimonious oxide and a little antimony :

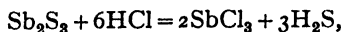


If this is warmed with hydrochloric acid the filtrate gives with H_2S an orange-red precipitate of Sb_2S_3 .

Halogen compounds of antimony.—Antimony forms two chlorides SbCl_3 and SbCl_5 . The trichloride is formed by heating excess of antimony in chlorine, by distilling antimony with mercuric chloride :



or by dissolving stibnite in hot concentrated hydrochloric acid :

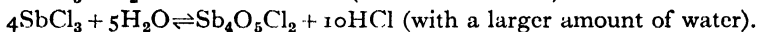
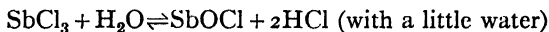


and distilling the solution, when hydrochloric acid comes over first and

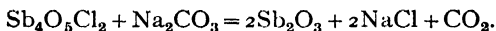
then antimony trichloride, which solidifies in the receiver as a soft white crystalline mass of *butter of antimony*.

The vapour density corresponds with SbCl_3 . Antimony trichloride is decomposed by water with deposition of white basic chlorides. It forms a clear solution with hydrochloric acid. Complex salts, *e.g.* NaSbCl_4 and K_2SbCl_5 , are formed with metallic chlorides.

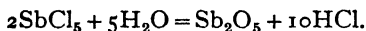
Antimonious oxychloride is precipitated as a white powder when a solution of the trichloride in hydrochloric acid is poured into water. The composition of the precipitate, known as *powder of Algaroth*, varies with the dilution but two definite oxychlorides are known :



By heating the oxychloride with water in a sealed tube or boiling it with sodium carbonate solution, antimony trioxide is formed :



Antimony pentachloride was discovered by Rose in 1825 and is formed when antimony burns in excess of chlorine or by the action of chlorine on the trichloride. It is a heavy yellow fuming liquid solidifying in a freezing mixture. The vapour is somewhat dissociated at the boiling point of 140° : $\text{SbCl}_5 \rightleftharpoons \text{SbCl}_3 + \text{Cl}_2$, but under reduced pressure the density corresponds with SbCl_5 . With ice-cold water crystalline hydrates are formed but hot water decomposes the pentachloride with formation of hydrated antimony pentoxide :



With concentrated hydrochloric acid and antimony pentachloride a fairly stable crystalline **chloroantimonic acid** $2\text{HSbCl}_6 \cdot 9\text{H}_2\text{O}$ is formed. This may also be prepared by passing chlorine through a solution of the trichloride in hydrochloric acid, and then adding excess of concentrated hydrochloric acid.

Other halogen compounds of antimony are the two **fluorides** SbF_3 and SbF_5 , the **bromide** SbBr_3 , and the **iodide** SbI_3 . Except SbF_5 (liquid) they are all solids.

Oxides of antimony.—Antimony forms three oxides: the **trioxide** Sb_2O_3 (or Sb_4O_6), the **dioxide** Sb_2O_4 (or SbO_2), and the **pentoxide** Sb_2O_5 . All are easily reduced by hydrogen or carbon on heating.

Antimony trioxide occurs native as *senarmonite* in cubic crystals, and also in rhombic crystals as *valentinite*. It is obtained as a pale buff-coloured powder by digesting antimony oxychloride SbOCl with a solution of sodium carbonate, or by passing steam over red-hot antimony.

From a hot solution in sodium carbonate both forms are deposited in white crystals. Antimony trioxide becomes yellow on heating but pale buff on cooling. It fuses at a dull-red heat and volatilises at a high temperature, the vapour density corresponding with Sb_4O_6 . It dissolves in hot concentrated sulphuric acid forming **antimony sulphate** $\text{Sb}_2(\text{SO}_4)_3$, readily in dilute hydrochloric acid to form the trichloride, in tartaric acid, and in alkalis forming salts called **metantimonites** e.g. $\text{NaSbO}_2, 3\text{H}_2\text{O}$.

Tartar emetic is an important preparation obtained by boiling oxide of antimony with water and cream of tartar (potassium hydrogen tartrate) and crystallising. It is usually supposed to contain the antimonyl radical SbO (present in SbOCl) and to be **potassium antimonyl tartrate** $2\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6, \text{H}_2\text{O}$. It is used as a mordant, as an emetic, and in the treatment of some tropical diseases.

Antimony dioxide is a white powder obtained on heating the trioxide or pentoxide to dull redness in air. At higher temperatures it decomposes into Sb_2O_3 and oxygen. Impure Sb_2O_4 is obtained by roasting stibnite; if the oxidation is incomplete the fused mass is known as *glass of antimony* and is used in colouring glass and porcelain yellow. Antimony dioxide appears to form salts when fused with alkalis.

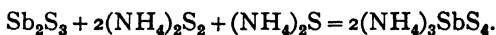
Antimony pentoxide is obtained as a light yellow powder by gently heating the solid produced by the repeated evaporation of antimony with concentrated nitric acid. It is almost insoluble in water.

When powdered antimony is added to potassium nitrate fused in a crucible white **potassium metantimoniate** KSbO_3 is formed, which is slowly soluble in boiling water. Dilute nitric acid precipitates from the solution a hydrated pentoxide (*antimonic acid*) which on gentle heating forms antimony pentoxide in a pure state.

The solution of potassium metantimoniate forms with sodium salts a white amorphous precipitate, which rapidly becomes crystalline and then consists of $\text{NaSb}(\text{OH})_6$ or $\text{NaSbO}_3, 3\text{H}_2\text{O}$, sparingly soluble in cold water and almost insoluble in alcohol. This is one of the least soluble sodium salts and its formation may be used as a test for sodium.

Sulphides of antimony.—The trisulphide Sb_2S_3 occurs native as *stibnite*. By precipitating a solution of antimony trichloride in hydrochloric acid with hydrogen sulphide, a *red* amorphous trisulphide is formed, which if dried and then heated in carbon dioxide gives off some free sulphur and forms the greyish-black crystalline modification. The red form is used as a pigment and in vulcanising red rubber. It is insoluble in dilute acids but dissolves in boiling concentrated hydrochloric acid (arsenic trisulphide is insoluble).

Precipitated antimony trisulphide is insoluble in warm ammonium carbonate solution (in which arsenic trisulphide is soluble) but dissolves in alkali sulphides and hot concentrated alkali solutions. Possibly thioantimonites, *e.g.* Na_3SbS_3 , are formed. A red precipitate of a mixture of Sb_2S_3 and Sb_2O_3 called *kermes mineral* is formed on diluting these solutions. By boiling antimony trisulphide with sodium hydroxide solution and sulphur, filtering and cooling, large pale-yellow crystals of sodium thioantimoniate $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$, or *Schlippe's salt*, are obtained. The corresponding ammonium salt is formed on dissolving antimony trisulphide in yellow ammonium sulphide :



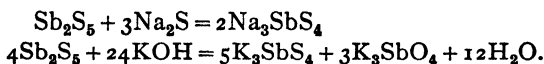
On acidifying the solutions an orange red precipitate, sometimes regarded as the pentasulphide but perhaps a mixture of antimony disulphide and sulphur, is formed, which is used as *golden sulphuret of antimony* in vulcanising rubber :



On heating alone or with water it decomposes into the black trisulphide and sulphur.

Antimony pentasulphide is precipitated as an orange powder when excess of hydrogen sulphide solution is added in the cold to a suspension of antimonious acid or to a solution containing antimonious acid and 12 per cent. of hydrochloric acid : $\text{As}_2\text{O}_5 + 5\text{H}_2\text{S} = \text{As}_2\text{S}_5 + 5\text{H}_2\text{O}.$

It readily dissolves in alkalis, even warm ammonia, and alkali sulphides, forming thioantimonates :



It also dissolves in sodium carbonate but not in ammonium carbonate.

The atomic weight of antimony was determined by various methods which gave numbers varying from 119.8 to 122.5. Dumas in 1859 obtained 121.8 by analysis of the trichloride but for many years the value 120.2 was accepted on the basis of Cooke's (1878-80) analyses of the chloride and bromide and the synthesis of the sulphide. The value 121.77, however, was found in 1921 by Willard and McAlpine from an analysis of the tribromide, and as the mass spectrograph shows the isotopes 121 and 123 the higher value is now accepted. It is practically identical with Dumas' figure. The valency is found from the atomic heat, and the density of the trichloride.

BISMUTH

History.—Bismuth (*wysmud*) is mentioned in German before 1500 and Agricola (who says it was unknown to the ancients) calls it *bisemutum* in his *Bermannus* (1530). The white basic nitrate was discovered by Libavius

in 1597 and was long used as a cosmetic ; bismuth chloride was discovered by Boyle in 1663. Bismuth was often confused with antimony and zinc but it was shown to be a separate metal by Pott in 1739 and Bergman afterwards investigated its compounds.

Occurrence.—Bismuth occurs somewhat sparingly, usually in the metallic or native condition associated with silver and cobalt ores in Bolivia, Saxony and Australia. The oxide Bi_2O_3 occurs as *bismuthite* or *bismuth ochre*, but the sulphide Bi_2S_3 , *bismuthine* or *bismuth glance*, is rare.

Metallurgy.—The metal is obtained from native bismuth by liquation, the ore being heated in sloping iron tubes when the fusible bismuth flows away. The oxide and sulphide ores, which usually contain cobalt and nickel, are first roasted when the trioxide Bi_2O_3 is formed. This is heated with charcoal, iron and a flux, when metallic bismuth fuses and collects below the cobalt and nickel arsenides. The crude bismuth is purified by dissolving in dilute nitric acid, pouring the solution of bismuth nitrate $\text{Bi}(\text{NO}_3)_3$ into water, calcining the basic nitrate precipitated, and reducing the oxide as before.

Properties.—Bismuth is a reddish-white brittle rather heavy metal which crystallises readily in large rhombohedral crystals like cubes, which are hollow and usually show beautiful green iridescent colours due to an oxide film. It is strongly diamagnetic.

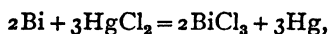
Bismuth has a low melting point and its alloys with some other metals have very low melting points (below 100°). The metal and its alloys expand when they solidify and the alloys are used as stereo-metal in printing, the cast being made just before solidification.

Wood's fusible metal contains bismuth, lead, tin and cadmium ; **Rose's metal** contains bismuth, lead and tin. Alloys of lead, bismuth and tin, melting slightly above 100° , are used in the construction of automatic sprinklers, which discharge water when the fusible metal plug is melted by a fire. Less fusible alloys are used as safety plugs in boilers.

Bismuth is only superficially oxidised in dry air and is only slowly attacked by water. When fused it is slowly oxidised to Bi_2O_3 , and when strongly heated it burns in air with a bluish-white flame, forming brown fumes of Bi_2O_3 , and it slowly decomposes steam liberating hydrogen. It is not attacked by dilute hydrochloric or sulphuric acids in the absence of oxygen but dilute nitric acid dissolves it forming the nitrate $\text{Bi}(\text{NO}_3)_3$. It also readily dissolves in *aqua regia* forming the trichloride BiCl_3 . Boiling concentrated sulphuric acid converts it into the sulphate $\text{Bi}_2(\text{SO}_4)_3$, sulphur dioxide being evolved. Bismuth combines readily with chlorine and sulphur.

Compounds of bismuth.—Traces of a gaseous hydride (BiH_3 ?) are formed by the action of acid on an alloy of magnesium and bismuth; a faint Marsh reaction is given by the gas.

Bismuth trichloride is formed as a soft white crystalline substance on passing excess of chlorine over bismuth, by heating bismuth with mercuric chloride :

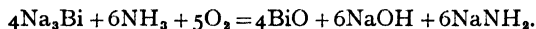


and by dissolving bismuth in *aqua regia*, evaporating and distilling. Its vapour density corresponds with the formula BiCl_3 . The solution in concentrated hydrochloric acid deposits crystals of **chlorobismuthous acid** H_2BiCl_5 , salts of which are known.

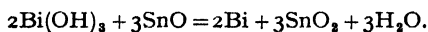
A solution of bismuth chloride when poured into water gives a white precipitate, which can be obtained crystalline, of **bismuth oxychloride** or **bismuthyl chloride** BiOCl . This contains the univalent **bismuthyl radical** $-\text{Bi}=\text{O}$, analogous to the antimonyl radical $-\text{Sb}=\text{O}$. It resembles silver chloride in becoming grey on exposure to light.

Bismuth hydroxide $\text{Bi}(\text{OH})_3$ is precipitated by alkalis from the solution of the nitrate as a white amorphous powder; it is insoluble in excess of alkali unless glycerol is added but is readily soluble in acids. When heated to 100° it forms $\text{BiO}(\text{OH})$, and on ignition leaves a pale yellow (greenish-grey when not quite pure and brown when hot) residue of **bismuth trioxide** Bi_2O_3 . This stable oxide of bismuth is obtained by heating bismuth nitrate or carbonate.

Bismuth monoxide, BiO , is apparently the only known compound of bivalent bismuth, $\text{Bi}=\text{O}$. It is a stable black powder formed by the action of oxygen gas on the alloy Na_3Bi in liquid ammonia :



It may be present in the black precipitate formed on adding a bismuth salt to a solution of sodium stannite (stannous chloride with excess of sodium hydroxide); it is often accompanied by a white precipitate of bismuth and stannous hydroxides and hence the reaction, which is used in the identification of bismuth (or stannous) salts, is called the "magpie test". It has been supposed, however, that the black colour in the precipitate is due to finely divided metallic bismuth :



Higher oxides of bismuth, Bi_2O_4 and Bi_2O_6 , are precipitated as reddish-brown powders on adding oxidising agents such as potassium ferricyanide or chlorine to alkaline suspensions of bismuth trioxide. On fusing bismuth trioxide with potassium hydroxide in air a brown mass of **potassium bismuthate**, perhaps KBiO_3 , is formed; it is hydrolysed by water and Bi_2O_3 is precipitated. The higher oxides of bismuth therefore show *acidic* properties.

Potassium bismuthate is used as an oxidising agent. The red precipitate formed by passing chlorine through a suspension of bismuth hydroxide in potassium hydroxide solution has been described as **bismuthic acid** HBiO_3 . It loses oxygen on heating.

Normal bismuth carbonate is not known but the white **basic carbonate** $2(\text{BiO})_2\text{CO}_3 \cdot \text{H}_2\text{O}$ is precipitated when sodium carbonate is added to a solution of the nitrate. It is given as a "bismuth meal" before X-radiology of the digestive tract, since it is opaque to X-rays.

The most important bismuth salt is the **nitrate**, obtained in crystals $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ by evaporating a solution of the metal, oxide or carbonate in warm dilute nitric acid. The solution when poured into a large volume of water deposits the white **basic nitrate** or "subnitrate" $\text{Bi}(\text{OH})_2\text{NO}_3$, used in medicine and as a cosmetic. The nitrate can be obtained in solution only if dilute nitric acid is added. The basic chloride and nitrate are readily distinguished from the antimony salts by adding a few crystals of tartaric acid and warming. The antimony salts dissolve but the bismuth salts are insoluble.

Bismuth sulphide Bi_2S_3 is obtained in crystals by fusing bismuth with sulphur, or as a brownish-black precipitate when hydrogen sulphide is passed into a solution of a bismuth salt. The precipitate dissolves in nitric acid and in boiling concentrated hydrochloric acid, but not in alkalis or yellow ammonium sulphide, since it does not like the sulphides of arsenic, antimony and tin form thio-salts in this way.

The **atomic weight of bismuth** was found by different methods with discordant results, *e.g.* 208.05 by Schneider in 1851 from the ratio $2\text{Bi} : \text{Bi}_2\text{O}_3$ and 210.7 by Dumas in 1859 from the analysis of the chloride. The value 209.02 was found by Hönigschmid in 1920 by analysis of the chloride. The valency is found from the atomic heat and the vapour density of the chloride.

CHAPTER XXX

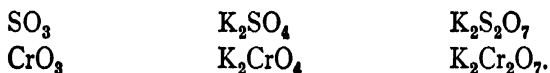
SULPHUR

Group VI of the Periodic System comprises nine elements :

Sub-group a (even series) : chromium, molybdenum, tungsten, uranium.

Sub-group b (odd series) : oxygen, sulphur, selenium, tellurium, polonium.

At first sight no obvious resemblances exist between the elements of the odd and even series. The latter are all metals. If we take sulphur as a representative of the odd series and chromium of the even series, a closer examination of their chemical properties shows many points of similarity. Both form acidic oxides RO_3 , the salts of which are isomorphous and have similar formulae:



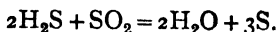
Both elements form stable oxychlorides RO_2Cl_2 hydrolysed by water, but there is no chloride of chromium corresponding with S_2Cl_2 . The stable chloride of chromium is CrCl_3 , corresponding with FeCl_3 and AlCl_3 , and chromium shows many resemblances to aluminium and iron. The metals chromium and iron are similar and the oxides Al_2O_3 , Cr_2O_3 and Fe_2O_3 are isomorphous. The three metals are in the same group in qualitative analysis. The analogy between iron and chromium is also seen in the formation of ferrates, e.g. K_2FeO_4 (red) and chromates, e.g. K_2CrO_4 (yellow). The compounds CrX_2 are closely analogous to ferrous salts and differ from the corresponding sulphur compounds.

SULPHUR

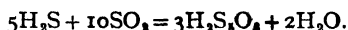
History.—Sulphur was perhaps known to the ancient Egyptians and Babylonians; it occurs in the Dead Sea region and is mentioned in the Bible. It was well known to the Greeks and Romans. The use of burning sulphur in fumigation is mentioned by Homer (c. 900 B.C.), the bleaching of textile fabrics by the fumes was carried out and sulphur was used medicinally. The alchemists regarded sulphur as the *principle of combustibility* and a constituent of metals. The phlogistonists considered it to be a compound of phlogiston and sulphuric acid. Lavoisier (1777) pointed out that it should be regarded as an element.

Occurrence.—Free sulphur occurs in large quantities in the volcanic region of Sicily, and in America in the southern States of Louisiana and Texas which now produce 80 per cent. of the total sulphur used in the world.

Sicilian sulphur is stratified with clay and rock, mostly gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, limestone and celestine SrSO_4 . It is found occasionally in large yellow transparent crystals, but usually in yellow or grey crystalline masses. The sulphur in the craters of extinct volcanoes may have been formed by the interaction of volcanic gases containing hydrogen sulphide and sulphur dioxide :



When dry hydrogen sulphide and sulphur dioxide gases are mixed by inverting one jar over the other and removing the plates, no action occurs. If a little water is introduced into the jars it becomes turbid, from separation of *yellow* sulphur. The reaction is complicated and pentathionic acid $\text{H}_2\text{S}_5\text{O}_6$ is also formed :



Since gypsum and calcium carbonate always occur in sulphur beds, the deposits of sulphur in Sicily have probably been formed by the reduction of gypsum by organic matter and bacteria :



Combined sulphur occurs as sulphides, many of which are important ores of metals : lead sulphide *galena* PbS , zinc sulphide *blende* ZnS , *copper pyrites* $\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3$, and *iron pyrites* FeS_2 ; and also as sulphates, e.g. *gypsum* $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Hydrogen sulphide occurs in volcanic gases and in some mineral springs. Sulphur dioxide occurs in volcanic gases. Some springs and rivers in America contain free sulphuric acid. Sulphur occurs in some kinds of organic matter; the blackening of silver spoons by eggs is due to this combined sulphur.

The extraction of native sulphur.—Native sulphur in Sicily, which contains 15 to 25 per cent. of sulphur, is stacked in lumps in brick kilns called *calcaroni*, built with air spaces on sloping hillsides and covered with powdered ore (Fig. 224). The ore is kindled at the top and the heat of combustion of about 30 per cent.

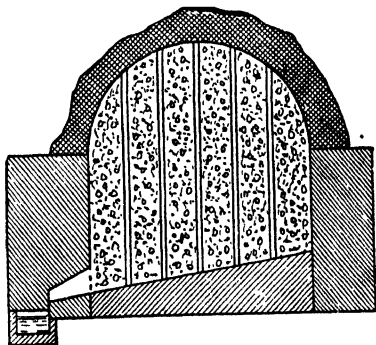


FIG. 224.—Sulphur kiln.

of the sulphur serves to melt the rest, which flows off into wooden moulds. The blocks so formed still contain 3 to 5 per cent. of the original rock.

An improved process uses the *Gill kiln* consisting of communicating closed brick chambers; hot gases from a chamber in which the sulphur has been melted out pass into an adjoining chamber and so economise heat.

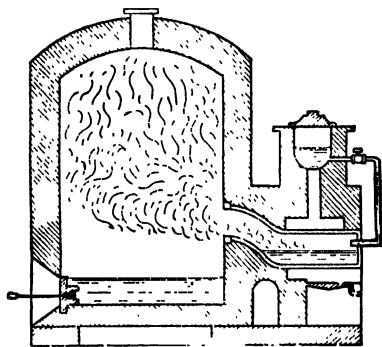


FIG. 225.—Refining of sulphur by distillation.

The crude sulphur is shipped from Sicily (where fuel is scarce) to Marseilles to be refined with the apparatus shown in Fig. 225. The sulphur fused in an iron pot flows into an iron retort. The sulphur vapour passes into a large brick-work chamber. At first it condenses on the cold walls as a light yellow powder of *flowers of sulphur*. As the walls become hot this melts

(unless it is removed) and runs down as a liquid to the bottom, whence it is tapped off into wooden moulds to form *roll sulphur* or *brimstone*.

American sulphur is extracted by the *Frasch process*. The deposit occurs below clay, quicksand and rock. A boring is made to the deposit and a "pump" of concentric pipes is sunk (Fig. 226). Down the outer pipe superheated water is pumped, which fuses the sulphur. Air is forced down the inner pipe, when an emulsion of molten sulphur and air-bubbles rises to the surface through the remaining annular space and passes to large wooden vats, where the sulphur of 99.5 per cent. purity solidifies and is ready for immediate use. It contains a little petroleum, which makes it rather difficult to burn.

Recovered sulphur.—Sulphur is extracted from Leblanc *alkali-waste* (containing insoluble calcium sulphide, CaS) by the *Chance-Claus process*.

Limekiln gas containing carbon dioxide is passed into a suspension of the waste in water in large iron vessels called *carbonators*. Hydrogen sulphide is evolved :

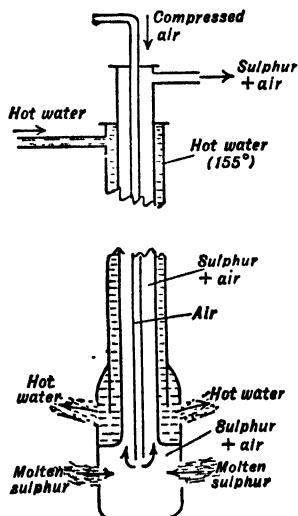
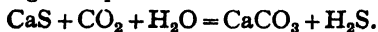
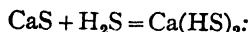
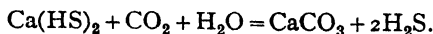


FIG. 226.—Frasch sulphur pump.

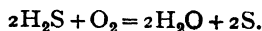
The gas is passed into a second carbonator where the hydrogen sulphide is absorbed, insoluble CaS passing into solution as calcium hydrosulphide



When all the CaS in the first vessel is decomposed the connections are changed so that the kiln gas passes directly into the second vessel. The $\text{Ca}(\text{HS})_2$ is then decomposed:



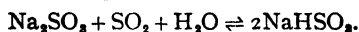
The gas is mixed with air, and passed over porous oxide of iron (acting as a catalyst) in the *Claus kiln*—a brickwork chamber with large brick condensing chambers and flues beyond. The oxide is heated to start the reaction which then proceeds automatically:



Coal contains pyrites FeS_2 , about half the sulphur of which during distillation in the manufacture of coal gas comes off as hydrogen sulphide and carbon disulphide. The sulphur of the hydrogen sulphide is recovered (p. 407) in iron oxide. The *spent oxide*, which contains about 50 per cent. of free sulphur, is then burnt in a current of air to produce sulphur dioxide, which is used to make sulphuric acid.

Some sulphur is recovered from the sulphur dioxide of metal roaster and smelter gases by dissolving in a suitable solvent, expelling the sulphur dioxide, and passing it over white-hot coke: $\text{SO}_2 + \text{C} = \text{CO}_2 + \text{S}$.

The solvent may be a cold solution of sodium sulphate containing aluminium chloride, and the gas is evolved on heating:



ALLOTROPIC FORMS OF SULPHUR

Sulphur is *dimorphous* and exists in two common crystalline forms: α -sulphur or rhombic sulphur and β -sulphur or monoclinic sulphur. There are also amorphous forms such as γ -sulphur or plastic sulphur.

Rhombic or α -sulphur crystallises in large pale-yellow transparent crystals (Fig. 227), giving a lemon-yellow powder, when a solution of

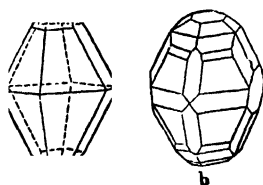


FIG. 227.—Crystals of rhombic sulphur.

roll sulphur in carbon disulphide is allowed to evaporate slowly in a dish covered with filter-paper. The density of α -sulphur is 2.06, its melting point is 112.8° . It is insoluble in water and only very slightly soluble in alcohol and ether, but is freely soluble in carbon disulphide, sulphur chloride (S_2Cl_2) and hot benzene and turpentine. *Rhombic sulphur is the form stable at the ordinary temperature and most other forms pass into it on standing.* Roll sulphur consists

almost entirely of rhombic sulphur; flowers of sulphur are principally composed of it (70 per cent.), but when genuine contain also a yellowish-white amorphous variety insoluble in carbon disulphide.

Monoclinic or β -sulphur is produced when fused sulphur is allowed to crystallise.

A large porcelain crucible is nearly filled with small pieces of roll sulphur, and heated *gently* on a sand-bath till the whole is just fused. It is allowed to cool until a crust forms on the surface. Two holes (one to admit air) are pierced in this crust with a pointed glass rod, and the still liquid portion poured out into a dry porcelain dish. On removing the crust, the inside of the crucible will be found to be lined with transparent needle-shaped crystals (Fig. 228) of β -sulphur, having usually a deeper yellow colour than α -sulphur. On standing for a few days the crystals become opaque brittle lemon-yellow aggregates of minute crystals of α -sulphur, although the original monoclinic form is preserved and the crystal is therefore called a *pseudomorph*. The transition from one form to the other is readily followed by the colour.

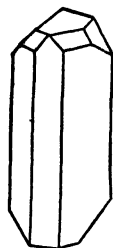


FIG. 228.—Crystal of monoclinic sulphur.

(Genuine Sicilian roll sulphur should be used for these experiments, since American sulphur may contain a trace of petroleum which results in dark coloured and unsatisfactory products.)

β -sulphur when quickly heated melts at 119° ; its density is 1.96. It is soluble in carbon disulphide and the solution on evaporation deposits α -sulphur.

The transformation of S_{β} into S_{α} is reversible; below 96° S_{α} is the stable form and above 96° S_{β} . This temperature is the **transition temperature** (or **transition point**) of sulphur. At the transition temperature both crystalline forms are in equilibrium: $S_{\alpha} \rightleftharpoons S_{\beta}$.

Substances like sulphur and tin (p. 446) which exist in *two* forms one of which is stable below a certain temperature and the other stable above it, are called **enantiotropic**; substances like phosphorus (p. 502) which exist only in *one* stable form, the other forms being unstable or metastable in all circumstances, are called **monotropic** (Greek *monos* one, *enantios* opposite, *tropos* habit).

A second variety of monoclinic sulphur is deposited in pearly leaflets from a hot solution of sulphur in benzene or turpentine on rapid cooling. This form, called **nacreous sulphur** by Gernez, is monotropic.

Sulphur boils at 444.6° and forms a deep red vapour which when strongly heated becomes yellow. Dumas (1832) found the vapour density at 524° to correspond with S_8 but the vapour was probably a mix-

ture of S_8 and S_2 ; at higher temperatures the density diminishes and at 1000° corresponds with S_2 . Nernst found that 45 per cent. of the S_2 molecules were broken up into atoms at 2000° : $S_2 \rightleftharpoons 2S$. Biltz (1888) and Bleier and Kohn (1900) found at lower temperatures (*e.g.* 193° at 2 mm.) densities higher than S_7 , and concluded that at lower temperatures the molecule is S_8 , partly dissociated even at the boiling point: $S_8 \rightleftharpoons 4S_2$. The lowering of vapour pressure of carbon disulphide by dissolved rhombic sulphur gives the formula S_8 but S_6 and S_4 have been given for S_ϕ and S_π (p. 547).

Equilibrium between rhombic and monoclinic sulphur.—In Fig. 229 OP is the vapour pressure curve of α -sulphur and represents the pressures of sulphur vapour in equilibrium with solid S_α at various temperatures. P is the transition point of α - and β -sulphur, where α - and β -sulphur and vapour are in equilibrium, and is a *triple point*; the three "phases" can co-exist only at one temperature and pressure. Q is the melting point of β -sulphur and is another triple point where β -sulphur, liquid and vapour are in equilibrium. QZ is the vapour pressure curve of liquid sulphur.

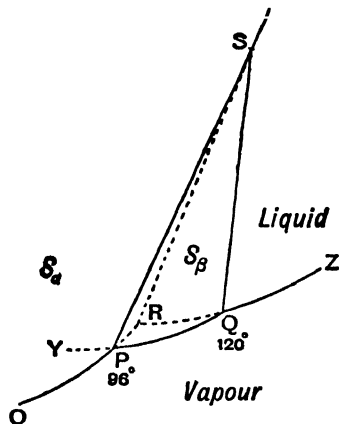


FIG. 229.—Vapour pressure diagram for sulphur.

If α -sulphur is heated rapidly the slow transition into β -sulphur at P will not occur but the curve PR will be followed to the point R , which is the melting point of α -sulphur (112.8°); at this point α -sulphur, liquid and vapour co-exist, so that R lies on the prolongation of the curve QZ . The point R lies in a *metastable* region since α -sulphur is not a stable phase above 96° . Below 96° α is stable and β unstable but above 96° β is stable and α unstable. But S_β may exist in a metastable condition below 96° because the change $S_\beta \rightarrow S_\alpha$ takes place only slowly. The prolongation of QP to Y expresses this fact, PY being the vapour pressure curve of S_β at temperatures below 96° . The melting points of α - and β -sulphur are raised by pressure but at different rates. This is represented by two lines starting from P and Q with different slopes and meeting ultimately at S (151° ; 1288 atm.) where S_α , S_β and liquid are in equilibrium. Above this point S_β cannot exist, the region of its stable existence being confined to the area PSQ . The areas defining the regions of existence of S_α , liquid and vapour are marked. If S_α is kept at a temperature between 96° and 112.8° for a long time and then heated, it will not melt at 112.8° but at 119° , since it has been converted into S_β .

Amorphous sulphur.—The changes which occur when sulphur is slowly heated to its boiling point are most remarkable.

When small pieces of genuine roll sulphur are slowly and carefully heated in a large test-tube, they melt to a clear-yellow mobile liquid. On cooling rapidly by pouring in water, S_8 is produced. If the temperature is now *gradually* raised and the tube shaken, the orange-red liquid *suddenly* becomes very viscous at 180° – 190° . At 230° the liquid is black and viscous. Beyond 230° the viscosity decreases but the colour remains dark, and the sulphur finally boils at 444.6° . If the boiling sulphur is allowed to cool *slowly* it passes through the above series of changes of colour and viscosity in the reverse order, solidifying as β -sulphur. But if the boiling liquid is *quickly* cooled by being poured into cold water it forms soft rubber-like transparent yellow threads, called plastic sulphur or γ -sulphur (Fig. 230).



FIG. 230.—Plastic sulphur.

Plastic sulphur has a density 1.92 and is insoluble in carbon disulphide. On standing for a few days it forms an opaque brittle pale-yellow solid consisting partly of rhombic sulphur but some of the solid is insoluble in carbon disulphide and consists of an amorphous variety called S_{μ} . At 100° the change takes place more rapidly.

An amorphous white sulphur remains as a pale yellow powder when genuine "flowers of sulphur" are extracted with carbon disulphide; it is also formed when a solution of sulphur in carbon disulphide is exposed to sunlight, or by the decomposition of sulphur chloride by water.

Powdered roll sulphur when boiled with milk of lime dissolves to form calcium pentasulphide and calcium thiosulphate:



The reddish-yellow solution is filtered. It was known to the early alchemists as *thion hutor* (the "divine" or "sulphurous" water). When it is acidified with dilute hydrochloric acid a white amorphous precipitate of *milk of sulphur* (*lac sulphuris*) is formed and hydrogen sulphide is evolved: $2\text{CaS}_5 + \text{CaS}_2\text{O}_3 + 6\text{HCl} = 3\text{CaCl}_2 + 3\text{H}_2\text{O} + 12\text{S}$.

Milk of sulphur, which is used medicinally, is soluble in carbon disulphide.

Colloidal sulphur is formed in the preparation of milk of sulphur: the filtered liquid is a turbid emulsion of sulphur. The milky liquid obtained by passing hydrogen sulphide into a solution of sulphur dioxide deposits on evaporation a gum-like mass, part of which is soluble in water (Debus, 1888).

Colloidal sulphur is obtained by the interaction of sodium thiosulphate solution and concentrated sulphuric acid. It is precipitated from the solution by addition of sodium chloride and centrifuging, and redissolves in water (Odén, 1913).

Two other varieties of sulphur have been described, viz., S_{π} and S_{ϕ} (or S_p). S_{π} is obtained when sulphur is heated to about 180° and rapidly cooled. Its solution in carbon disulphide is deep yellow. S_{ϕ} is said to be produced when a cold solution of sodium thiosulphate is added to concentrated hydrochloric acid at 0° and the mixture shaken with toluene. After a short time orange-yellow crystals of S_{ϕ} are stated to separate from the toluene. The solutions of S_{ϕ} are yellow but not so strongly as those of S_{π} .

Uses of sulphur.—*Crude sulphur* is used for making sulphur dioxide and thence sulphuric acid, for bisulphites for paper manufacture, and carbon disulphide. *Refined sulphur* is used in medicine, in the form of powder as a fungicide, and in the preparation of gunpowder, matches, fireworks and dyes. Sulphur is also used in large quantities for vulcanising rubber.

For use in dressing vines (to prevent the growth of the fungus *Oidium*), sulphur is finely ground between millstones and sieved through silk. By blowing a current of air through the mill, the very finest particles ("winnowed sulphur") are carried off and are retained by cloth filters.

HYDROGEN SULPHIDE

Sulphur and hydrogen form a gaseous compound H_2S , called hydrogen sulphide (or "sulphuretted hydrogen"), and several liquid compounds, from H_2S_2 to H_2S_8 .

History.—Although hydrogen sulphide was known by its smell to the alchemists the gas was first carefully examined by Scheele in 1777; he proved that it is a compound of hydrogen and sulphur.

Occurrence.—Hydrogen sulphide occurs in volcanic gases and in some mineral waters, e.g. of Harrogate, Aix-la-Chapelle, etc. It is formed in the putrefaction of organic substances containing sulphur and contributes to the smell of rotten eggs and sewer gas.

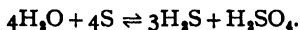
Preparation.—When hydrogen is passed over boiling sulphur in a bulb-tube the issuing gas contains a small amount (1 or 2 per cent.) of hydrogen sulphide and blackens lead acetate paper owing to the formation

of lead sulphide PbS. If pure hydrogen sulphide is heated partial decomposition occurs with deposition of sulphur, hence the reaction is reversible :



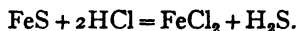
The pure gas is prepared synthetically in presence of pumice as a catalyst at 600° , when the reaction is practically complete.

Traces of hydrogen sulphide are formed when sulphur is boiled with water :



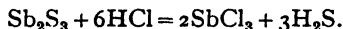
The gas is formed when heavy naphtha (sp. gr. 0.9) is dropped into boiling sulphur in a flask, and is evolved in a regular stream on heating a mixture of powdered sulphur, paraffin wax and ignited asbestos. Hydrogen in the hydrocarbons is substituted by sulphur (S replaces 2H).

Hydrogen sulphide is usually prepared in the laboratory by the action of dilute sulphuric acid or better hydrochloric acid (1 : 3) on ferrous sulphide in a Kipp's apparatus :

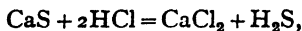


The gas is washed with a little water before use. Since the ferrous sulphide contains free iron the gas contains hydrogen, which does not interfere with its use in qualitative analysis.

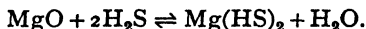
Hydrogen sulphide free from hydrogen is obtained by heating powdered antimony sulphide (*stibnite*) with concentrated hydrochloric acid :



The pure gas is obtained from pure zinc sulphide or calcium sulphide and hydrochloric acid :



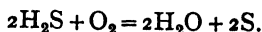
or by heating to 60° a solution of magnesium hydrosulphide obtained by passing the impure gas through magnesia suspended in water :



Hydrogen sulphide may be dried with calcium chloride or phosphorus pentoxide; it is decomposed by concentrated sulphuric acid. It is collected in dry jars by displacement (it is 1.2 times as heavy as air) since it is soluble in water (3.4 vols. to 1 vol. water at 10°) and tarnishes mercury unless it is dry and free from oxygen.

Properties.—Hydrogen sulphide is a colourless gas with a powerful odour of rotten eggs (decaying albumin evolves H_2S) and is poisonous; it liquefies fairly easily to a colourless liquid and at lower temperatures forms a transparent solid.

The aqueous solution is a feeble acid ; the gas is completely expelled by boiling, and on standing in air the solution becomes turbid owing to oxidation and deposition of sulphur :

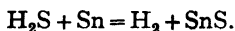


This is retarded by the addition of 1 c.c. of glycerin to 50 c.c. of saturated solution. In decinormal solution 0.1 per cent. is ionised to $\text{H}^+ + \text{HS}'$; the further stage to S'' is very slight :

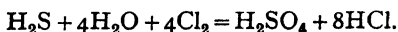
$$\begin{aligned} [\text{H}^+][\text{HS}']/[\text{H}_2\text{S}] &= 9.1 \times 10^{-8} \\ [\text{H}^+][\text{S}'']/[\text{HS}'] &= 1.2 \times 10^{-15}. \end{aligned}$$

A solid crystalline hydrate H_2S , $6\text{H}_2\text{O}$ is formed at low temperatures.

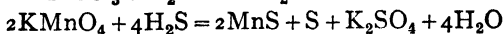
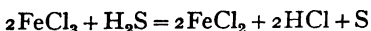
The gas is decomposed into its elements by electric sparks or by a heated platinum spiral : $\text{H}_2\text{S} = \text{H}_2 + \text{S}$, and by heated tin or lead, giving its own volume of hydrogen : hence the formula is H_2S_x . The density of the gas corresponds with the molecular weight 34, hence the weight of sulphur in the molecular weight is 32, the atomic weight, $\therefore x = 1$, and the formula is H_2S :



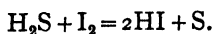
Chlorine decomposes hydrogen sulphide and sulphur is deposited : $\text{H}_2\text{S} + \text{Cl}_2 = 2\text{HCl} + \text{S}$, but sulphur chloride is also formed. A solution of hydrogen sulphide with a large excess of chlorine water slowly forms sulphuric acid :



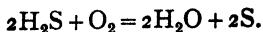
Hydrogen sulphide, which is easily oxidised, is a reducing agent in aqueous or alcoholic solution. It reduces solutions of ferric chloride, potassium permanganate and potassium dichromate :



Hydrogen sulphide may be determined by titration in dilute solution with iodine solution :



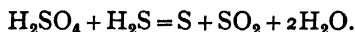
The gas kindled in air or oxygen burns with a blue flame ; it is completely dissociated in the interior of the flame, which deposits sulphur on a cold porcelain dish. If the gas in a glass cylinder is kindled at the mouth a deposit of sulphur is formed on the inside of the jar, owing to the deficiency of oxygen :



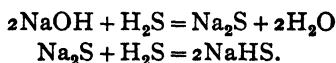
With a plentiful supply of oxygen, as when the gas burns at a jet, sulphur dioxide is formed : $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{H}_2\text{O} + 2\text{SO}_2$.

A mixture of 2 vols. of H_2S and 3 vols. of oxygen explodes violently when kindled.

The gas decomposes concentrated sulphuric acid :



It is absorbed by solutions of alkali hydroxides and by slaked lime, forming sulphides and (with excess of H_2S) hydrosulphides :



Fuming nitric acid reacts violently with the gas, ignition and perhaps explosion occurring. Very dilute (5 per cent.) nitric acid is not affected ; with more concentrated acid (43 per cent.) the products are sulphuric acid, sulphur, ammonia, nitrous acid, nitric oxide and nitrous oxide. A solution containing 23 per cent. of nitric acid and 15 per cent. of sulphuric acid is inert towards the gas, whether prepared by mixing or by the reaction itself.

The gas or its solution (*e.g.* in mineral waters) may be detected by the black coloration due to lead sulphide PbS , produced with lead acetate. If alkali sulphides are present they give a purple colour, not produced by free H_2S , with a freshly-prepared solution of (sodium nitroprusside $\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5$)

Precipitation of sulphides.—Hydrogen sulphide precipitates sulphides from solutions of salts of many metals. These sulphides often have characteristic colours, and hydrogen sulphide is used as a reagent in qualitative analysis.*

Some (Group II) sulphides are precipitated from solutions acidified with hydrochloric acid : copper, lead, mercuric and bismuth salts all give *black* sulphides (bismuth, brownish-black), CuS , PbS , HgS , Bi_2S_3 ; cadmium, tin (stannic) and arsenic give *yellow* sulphides, CdS , SnS_2 , As_2S_3 ; antimony gives an *orange-red* sulphide Sb_2S_3 ; tin (stannous) a *brown* sulphide SnS .

In some cases (Group IV) metals are precipitated only in *alkaline* solutions. An alkali sulphide, *e.g.* ammonium sulphide, may be used. The precipitates are black (FeS , CoS , NiS), white (ZnS) and flesh-coloured or greenish (MnS).

If the sulphides are very sparingly soluble (PbS , CuS , HgS , As_2S_3 , Sb_2S_3 , etc.) the concentration of S'' ions formed from them is never large

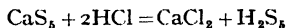
* On the theory of sulphide precipitation, see Partington and Stratton, *Intermediate Chemical Calculations*, ch. xii.

enough, even with relatively high concentrations of H^+ ions, to give an ionic product $[H']^2 \times [S'']$ exceeding the solubility product of H_2S , so that the latter cannot be formed. In other words, the sulphides are precipitated even in the presence of acids. Cadmium sulphide CdS occupies an intermediate position; if the acid concentration is greater than $1.3N$ it is not precipitated. Solutions of zinc salts are incompletely precipitated, since the acid formed leads to an equilibrium state (p. 354). Sulphides of some metals (FeS , ZnS , MnS) are precipitated in alkaline solution, because then practically no H^+ ions are formed. The metals of the alkalis and alkaline earths are not precipitated, because their sulphides are soluble in water (Na_2S , K_2S) or in a solution of hydrogen sulphide ($CaS + H_2S \rightleftharpoons Ca(SH)_2$). Aluminium and chromium salts give precipitates of *hydroxides* with ammonium sulphide, since their sulphides are completely hydrolysed by water: $2Al''' + 3S'' + 6H_2O = 2Al(OH)_3 + 3H_2S$.

Hydrogen persulphides.—If an acid is added to the yellow *thion hudor* (p. 547) hydrogen sulphide is evolved and white colloidal sulphur is formed, slowly depositing as milk of sulphur:



Scheele (1777) found, however, that if the calcium sulphide solution is poured in a thin stream into cold fairly concentrated hydrochloric acid, with constant stirring, a yellow oil separates. Thenard (1831) regarded this as H_2S_2 , analogous to H_2O_2 , but Rebs (1888) as H_2S_8 . By fractional distillation in vacuum the oil gives the liquid hydrides H_2S_2 , H_2S_3 , H_2S_4 , H_2S_5 , and H_2S_6 . The oil contains mainly H_2S_6 and perhaps H_2S_8 :



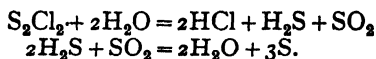
and the other sulphides are formed from these during the distillation. The hydrogen persulphides are unstable and decompose on warming into hydrogen sulphide and sulphur. The formation of hydrogen persulphide may be shown by pouring 100 c.c. of *thion hudor* in a thin stream with vigorous stirring into 250 c.c. of 1 : 1 hydrochloric acid in a beaker. A milky liquid is formed which bleaches litmus paper and on standing in a separating funnel the liquid deposits a yellow oil of crude hydrogen persulphide.

COMPOUNDS OF SULPHUR WITH HALOGENS

Sulphur burns spontaneously in fluorine to form a stable gaseous **hexafluoride** SF_6 . As well as SF_6 , a little S_2F_{10} is formed. In SF_6 sulphur has its maximum valency of 6. The gas is remarkably inert, resisting fused potassium hydroxide and red-hot copper, but it is decomposed by boiling sodium: $SF_6 + 8Na = Na_2S + 6NaF$, and by hydrogensulphide: $SF_6 + 3H_2S = 6HF + 4S$.

Sulphur monochloride S_2Cl_2 is prepared by passing dry chlorine over sulphur fused in a retort. A red liquid distils over into a cooled receiver. By distilling over powdered sulphur, or in contact with active charcoal, a clear amber-coloured liquid boiling at 138° is obtained. Sulphur mono-

chloride has a vapour density which corresponds with S_2Cl_2 . It has a most disagreeable pungent odour and fumes in moist air owing to hydrolysis :



The liquid is only slowly decomposed by water ; hydrochloric acid and sulphur are formed together with various oxy-acids of sulphur (*e.g.* pentathionic acid). Metals decompose it on heating, forming chlorides and sulphides. Sulphur chloride dissolves sulphur readily.

By the action of excess of chlorine, the unstable red dichloride SCl_2 and at low temperatures the brown tetrachloride SCl_4 are formed. Both decompose on warming into chlorine and S_2Cl_2 . Sulphur monobromide S_2Br_2 is a red liquid formed from its elements. No iodide is known.

COMPOUNDS OF SULPHUR AND OXYGEN

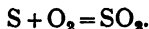
Sulphur forms two important oxides, gaseous sulphur dioxide SO_2 and solid sulphur trioxide SO_3 . It forms a large number of oxy-acids of which the most important are sulphurous acid H_2SO_3 , known only in solution and in the form of salts, and sulphuric acid H_2SO_4 .

SULPHUR DIOXIDE

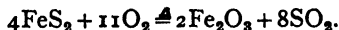
History.—Homer refers to the use of burning sulphur in fumigation and Pliny states that the fumes were used for purifying cloth (*i.e.* bleaching). The alchemists thought the pungent fumes were oil of vitriol, but Stahl (1702) showed that they gave peculiar salts with alkalis and since they stood halfway between sulphuric (vitriolic) acid and sulphur (the latter regarded as sulphuric acid + phlogiston), his followers called the acid *phlogisticated vitriolic acid*. Priestley (1774) obtained gaseous sulphur dioxide by heating concentrated sulphuric acid with mercury and collected it over mercury. He called it *vitriolic acid air*. Its composition was determined by Lavoisier in 1777.

Occurrence.—Sulphur dioxide occurs in volcanic gases and traces are present in the atmosphere, being derived from the combustion of iron pyrites contained in coal and in various metallurgical and chemical processes.

Preparation.—Sulphur dioxide is formed (together with a little trioxide) when sulphur burns in oxygen :

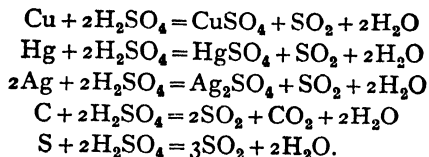


It is also formed (*mixed with atmospheric nitrogen*) * when sulphur or iron pyrites burns in air :



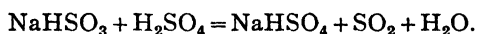
* It is a very common error to give this as a laboratory preparation of sulphur dioxide.

In the laboratory sulphur dioxide gas is usually made by heating concentrated sulphuric acid with copper turnings. The acid is also reduced when heated with mercury, silver or charcoal ; the reaction with sulphur is very slow :



Copper turnings covered with concentrated sulphuric acid are heated on wire gauze in a flask fitted with a thistle funnel. The mixture becomes dark and gas is evolved with effervescence. When this occurs the flame is lowered or removed. The gas is collected by downward displacement or over mercury. It may be dried by concentrated sulphuric acid (or calcium chloride, or phosphorus pentoxide). After cooling the residue in the flask may be warmed with water, and the solution filtered, evaporated and set aside. Deep-blue crystals of copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (*blue vitriol*) separate.

Sulphur dioxide is evolved by the action of acids on sulphites or acid sulphites, e.g. by dropping concentrated sulphuric acid into a concentrated solution of sodium hydrogen sulphite :



Sulphur dioxide is also formed in a number of reactions when sulphides or sulphur are exposed to oxidising agents. On the large scale the mixture of sulphur dioxide and nitrogen formed by burning sulphur or pyrites in air is washed with water and the sulphur dioxide expelled from the solution by heating ; the dry gas is then liquefied by compression. Liquid sulphur dioxide is sold in glass siphons or in steel containers. Sulphur dioxide is used in bleaching wool or straw, as a disinfectant, in making sulphites for the paper industry and in making sulphuric acid. Liquid sulphur dioxide has been used in purifying petroleum products.

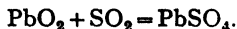
Properties.—Sulphur dioxide is a colourless gas $2\frac{1}{2}$ times as heavy as air, with a suffocating smell well known as that of burning sulphur. It is easily liquefied by compression ($2\frac{1}{2}$ atm. at 15°) or cooling to form a colourless liquid.

The liquid is easily prepared by passing the gas through a glass spiral immersed in a mixture of pounded ice and salt (Fig. 209) and is collected in a strong tube with the neck drawn off, immersed in a freezing mixture. The neck may be sealed whilst the tube remains cooled.

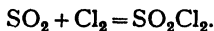
Sulphur dioxide gas does not support combustion in the ordinary sense, but heated potassium burns in it, forming sulphite and thiosulphate :



Finely divided tin and iron also burn in the gas when heated, forming mixtures of oxides and sulphides. Pure lead dioxide warmed in a bulb tube becomes incandescent when sulphur dioxide is passed over it and white lead sulphate is formed :



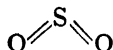
Sulphur dioxide in sunlight combines with chlorine forming **sulphuryl chloride**, a volatile fuming liquid, easily hydrolysed by water (p. 564) :



The *formula* of sulphur dioxide is found by burning sulphur in oxygen, when the volume is unchanged.

A small piece of sulphur in a metal spoon is kindled in dry oxygen over dry mercury in the apparatus shown in Fig. 186. When the apparatus is cool, the mercury levels are unchanged.

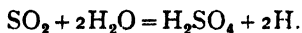
Hence sulphur dioxide contains its own volume of oxygen, and the formula is S_xO_2 . The density shows that the molecular weight is 64. This contains one molecule of oxygen and hence $64 - 32 = 32$ parts or one atom of sulphur, hence the formula is SO_2 . The structural formula is



the molecule being bent. The carbon dioxide molecule $O=C=O$ is linear.

Sulphurous acid.—Sulphur dioxide is freely soluble in water (45 vols. to 1 of water at 15°) forming an acid liquid smelling strongly of the gas. This probably contains the unstable **sulphurous acid** H_2SO_3 , which has never been isolated. On boiling all the sulphur dioxide is evolved. When the saturated solution is strongly cooled crystals of the hydrate $SO_2 \cdot 6H_2O$ separate. The solution when heated in a sealed tube at 150° deposits sulphur : $3H_2SO_3 = 2H_2SO_4 + H_2O + S$.

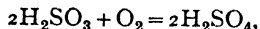
The solution of sulphurous acid possesses bleaching properties ; moistened wool, straw for hats, and other materials which would be injured by chlorine, are bleached on exposure to sulphur dioxide or the fumes of burning sulphur. This property, which is mentioned by Pliny, has been explained by two theories : (i) the formation of colourless addition compounds with the colouring matters ; (ii) the reduction of the colours to colourless compounds, possibly by nascent hydrogen :



A dilute fuchsine ("magenta") solution is bleached by sulphur dioxide. On boiling the colour is restored.

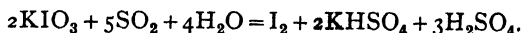
Red roses may be bleached by wetting them and suspending in a bell-jar over burning sulphur; on dipping the flowers into dilute sulphuric acid the colour is restored.

Sulphurous acid solution is slowly oxidised by atmospheric oxygen to sulphuric acid :

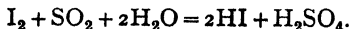


but the rate of oxidation is much reduced by adding glycerol or other substances.

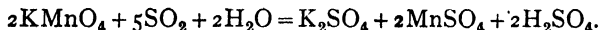
Sulphurous acid and sulphites are *reducing agents*; they liberate iodine from potassium iodate :



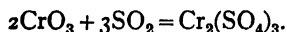
The titration of the liberated iodine is a means of estimation of SO_2 in flue-gases or sulphites in solution. With excess of sulphur dioxide the iodine is reduced :



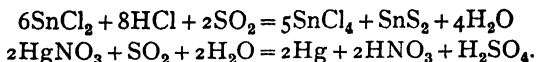
Sulphur dioxide reduces mercuric chloride to mercurous chloride (p. 361). It decolorises a neutral solution of potassium permanganate :



A piece of paper dipped in acidified potassium dichromate solution (yellow) becomes green in sulphur dioxide :



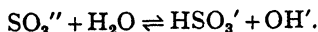
Sulphurous acid solution evolves hydrogen with magnesium. Sulphur dioxide and sulphites are reduced to hydrogen sulphide by zinc and hydrochloric acid; they precipitate *stannic* sulphide from a solution of *stannous* chloride in hydrochloric acid, and mercury from a solution of mercurous nitrate :



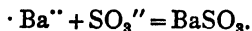
Sulphites.—Sulphurous acid is dibasic and forms two series of salts, which theoretically would have the formulae MHSO_3 and M_2SO_3 . These salts may be prepared by the following experiment.

Divide a solution of sodium hydroxide into two equal parts. Saturate one with SO_2 producing a solution of sodium hydrogen sulphite, NaHSO_3 . This is acid owing to the reaction : $\text{HSO}_3' \rightleftharpoons \text{SO}_3'' + \text{H}'$. Mix this with the other half of the sodium hydroxide and evaporate. Crystals of normal sodium sulphite $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ are produced on cooling.

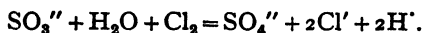
Sodium sulphite forms a slightly alkaline solution owing to hydrolysis :



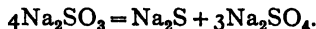
It gives a white precipitate of **barium sulphite**, *soluble in hydrochloric acid*, on addition of barium chloride :



If chlorine- or bromine-water is added a white precipitate of **barium sulphate**, *insoluble in hydrochloric acid*, is formed :

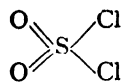
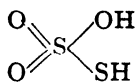
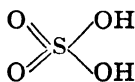
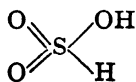


If a solution of sodium hydrogen sulphite is evaporated with excess of sulphur dioxide, or if sulphur dioxide is passed over crystals of sodium carbonate monohydrate $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, the solid **sodium disulphite** (or *meta-bisulphite*) $\text{Na}_2\text{S}_2\text{O}_5$ (*i.e.* $\text{Na}_2\text{O} \cdot 2\text{SO}_2$), used in photography, is formed. On heating dry sodium sulphite the sulphate and sulphide are formed :



The disulphite on heating first decomposes into Na_2SO_3 and SO_2 , and the Na_2SO_3 then decomposes as above. The simple acid sulphites *e.g.* NaHSO_3 do not appear to exist in the solid form. The commercial solid "bisulphite" is probably mostly $\text{Na}_2\text{S}_2\text{O}_5$.

The structural formula of sulphurous acid is probably unsymmetrical since the acid or its salts readily combine with oxygen or sulphur to form sulphates or thiosulphates, respectively :



Thionyl chloride, prepared by the action of sulphur dioxide on phosphorus pentachloride :



has the formula shown above.

SULPHUR TRIOXIDE

Sulphur trioxide is formed by the direct union of the gaseous dioxide with ozone (Brodie) : $3\text{SO}_2 + \text{O}_3 = 3\text{SO}_3$. It is prepared by passing a mixture of sulphur dioxide and oxygen over a catalyst such as heated platinised asbestos : $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$.

Sulphur dioxide and oxygen gases are passed through sulphuric acid in a wash bottle to dry them and then over dry platinised asbestos heated in a hard glass tube. Sulphur trioxide is produced which condenses to colourless crystals in a dry test-tube cooled in a freezing mixture (Fig. 231).

A state of equilibrium is set up since the reaction is reversible and excess of oxygen, according to the law of mass action, favours the formation of the trioxide :

$$[\text{SO}_3]^2/[\text{SO}_2]^2[\text{O}_2] = K.$$

Other catalysts such as ferric oxide and vanadium pentoxide can be used instead of platinum, but the temperature must then be higher, and since the reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ is exothermic the equilibrium yield of SO_3 is smaller at higher temperatures (p. 231). At lower temperatures the reaction is too slow. The best results are obtained by working at $400\text{--}450^\circ$ with platinum and using an excess of oxygen, which favours the yield of SO_3 by mass action.

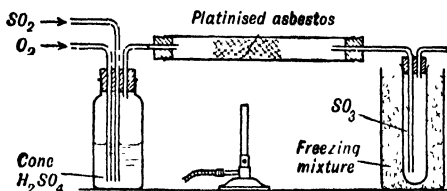
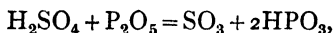
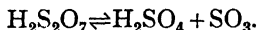


FIG. 231.—Preparation of sulphur trioxide.

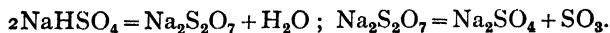
Sulphur trioxide is also produced by heating concentrated sulphuric acid with excess of phosphorus pentoxide :



or most conveniently on the small scale by distilling fuming sulphuric acid in a retort and collecting the trioxide in a perfectly dry receiver cooled in a freezing mixture :



If sodium hydrogen sulphate is heated at 300° it forms the pyrosulphate and this evolves sulphur trioxide at a bright-red heat :



Sulphur trioxide exists in more than one modification. The liquid first formed in the cooled tube solidifies on cooling to transparent crystals, but these on standing (at least in presence of a trace of moisture) soon form silky asbestos-like crystals, and there may be two forms of this.

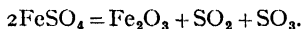
When passed through a red-hot tube sulphur trioxide vapour is decomposed, giving 2 vols. of SO_2 (absorbed by alkali) and 1 vol. of O_2 . This shows that the formula is $(\text{SO}_3)_x$. The vapour density of the trioxide shows that $x = 1$, hence the formula is SO_3 : $2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$.

Sulphur trioxide greedily absorbs moisture from the air, giving dense white fumes of droplets of sulphuric acid : $\text{H}_2\text{O} + \text{SO}_3 = \text{H}_2\text{SO}_4$. It dissolves in water with a loud hissing noise and considerable evolution of heat, but dissolves readily and quietly in concentrated sulphuric acid ; the fuming acid so obtained solidifies on cooling to colourless crystals of **disulphuric** or **pyrosulphuric acid** $\text{H}_2\text{S}_2\text{O}_7$. Sulphur trioxide reacts violently with baryta, the mass becoming incandescent : $\text{SO}_3 + \text{BaO} = \text{BaSO}_4$.

The manufacture of sulphur trioxide will be described under the contact process for making sulphuric acid (p. 562).

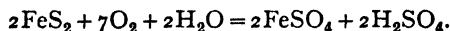
SULPHURIC ACID

History.—Sulphuric acid or *oil of vitriol* is mentioned by the alchemists, who obtained it by distilling *green vitriol* (ferrous sulphate) :



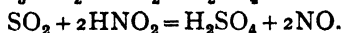
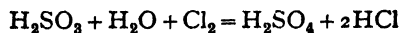
Lemery in 1675 made it by deflagrating a mixture of sulphur and nitre over a dish of water under a glass bell, and a small works using this process was established in 1740 by Ward at Richmond. The acid obtained was called oil of vitriol *per campanam*. Roebuck in 1746 in Birmingham, and in 1749 at Prestonpans, replaced the fragile glass vessels by lead chambers 6 ft. wide, and these were enlarged in later works. A continuous process in which the sulphur dioxide was produced from sulphur in separate burners and admitted with nitrous fumes, air, and steam to the chambers was introduced by Holker into the French works of Chaptal in 1810. The use of pyrites and the invention of the Gay-Lussac and Glover towers led to the modern industry. The chamber process is still largely used for making ordinary (not fuming) sulphuric acid.

Occurrence.—Free sulphuric acid occurs in traces in the rain water of towns where coal is burnt and is found in some rivers and springs which have been in contact with beds of pyrites :

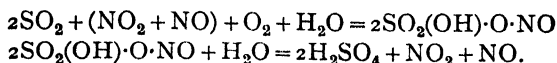


In combination as sulphates it is very common.

Preparation.—Sulphuric acid is formed from sulphur trioxide and water : $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$. Moistened flowers of sulphur when exposed to air are slowly oxidised to sulphuric acid. Sulphurous acid solution oxidises slowly when exposed to air : $2\text{H}_2\text{SO}_3 + \text{O}_2 = 2\text{H}_2\text{SO}_4$. Oxidation occurs more rapidly when hydrogen peroxide is shaken in a jar of sulphur dioxide : $\text{SO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_4$, or when chlorine water, bromine water or nitrous acid is added :

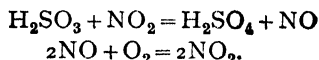


Sulphuric acid is manufactured by the **lead chamber process**. The reactions in the lead chambers occur between sulphur dioxide, oxygen (air), steam (or water-spray), and oxides of nitrogen ("nitrous fumes"). Clement and Desormes in 1806 discovered an intermediate compound in the reaction, viz. **nitrososulphuric acid** ("chamber crystals"), sulphuric acid $\text{HO}\cdot\text{SO}_2\cdot\text{OH}$ in which H is replaced by the nitroso-group NO. It may be formed and decomposed alternately in the chambers :



The nitrous gas or mixture $\text{NO}_2 + \text{NO}$ therefore acts in a cyclic manner, *i.e.* as a catalyst (see p. 110).

A simpler explanation assumes that sulphurous acid * is oxidised to sulphuric acid by nitrogen dioxide, and the nitric oxide formed is then reoxidised by atmospheric oxygen :



The lead chamber reactions may be illustrated by the following experiment.

A dry 6-litre flask *A* (Fig. 232) is fitted with tubes as shown. Three of the tubes are connected with wash-bottles containing concentrated sulphuric acid. One of these is connected with a siphon of liquid SO_2 , one to a gas-holder containing oxygen, the third to a gas-holder containing nitric oxide, and the fourth with a small flask *B* containing water which may be heated, and through which oxygen may be bubbled. A stream of dry oxygen is first passed through *A*. Nitric oxide is then passed in and forms

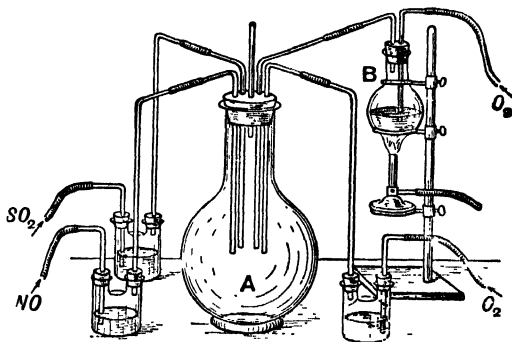


FIG. 232.—Experiment illustrating the chamber process.

red higher oxides of nitrogen. Sulphur dioxide is then passed in at the same rate as the nitric oxide and after a short time a current of oxygen is passed through the hot water in *B* to carry moisture into the globe. Colourless star-shaped crystals of nitrososulphuric acid form

* Sulphur dioxide in absence of water is not oxidised to sulphur trioxide by NO_2 but undergoes a different reaction; according to Michaelis (1874) and Manchot (1929) nitrosylsulphuric anhydride $\text{S}_2\text{N}_2\text{O}_3$ is formed.

on the inside of the globe and the colour of the gas becomes paler. The gas is swept out by a rapid current of oxygen and the water in *B* is boiled. When the steam comes in contact with the crystals they dissolve with effervescence, producing red oxides of nitrogen and fairly concentrated sulphuric runs down to the bottom of the flask. If insufficient water is used in the first stage, a white powdery deposit is formed which gives purple drops in contact with steam.

Manufacture of sulphuric acid by the lead chamber process.*—On the large scale (Fig. 233) iron pyrites is burnt in brick furnaces called

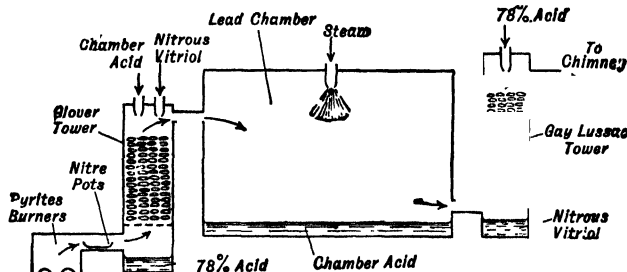


FIG. 233.—Sulphuric acid chamber plant (diagrammatic).

pyrites burners, the supply of air being regulated by sliding doors above and below the bed of pyrites. The pyrites burners are arranged in sets with a communicating flue. Pyrites powder or "spent oxide" (p. 543) is burnt in rotary kilns consisting of iron cylinders lined with firebrick, with a series of shelves so arranged that the ore is raked from shelf to shelf by rotating scrapers until the burnt ore is discharged at the bottom. Sulphur is burnt in large inclined rotating cylinders or other type of special burner.

The burner gas (7 per cent. of SO_2 , 10 per cent. of O_2 , 83 per cent. of N_2) passes to a dust-catcher containing baffle-walls, and then through a nitre-oven in which pots containing sodium nitrate and sulphuric acid are placed. These supply the oxides of nitrogen to make up losses from the plant. In modern plants, the oxides of nitrogen are supplied by the oxidation of ammonia (p. 484).

From the nitre-oven the hot gases pass into the Glover tower, a squat lead tower 20 to 30 ft. high and 6 to 8 ft. diameter lined with acid-resisting bricks and packed with flints resting on an arch. Down this tower two streams of acid pass from tanks at the top, one of acid (65 to 70 per cent. H_2SO_4) from the lead chambers and the other of stronger acid (78 per cent. H_2SO_4) containing oxides of nitrogen (in the form of nitrososulphuric acid) from the Gay-Lussac tower. The functions of the Glover tower are: (a) to cool the burner gases before they enter the chambers; (b) to denitrate the acid from the Gay-Lussac tower by dilution with chamber acid and heating, and by reaction with

* On the chamber and contact processes see Partington, *The Alkali Industry*, 1925; and Fairlie, *Manufacture of Sulphuric Acid*, New York, 1934.

sulphur dioxide; (c) to concentrate the chamber acid to about 78 per cent. H_2SO_4 and at the same time provide part of the steam for the chambers. About 25 per cent. of the total acid made is formed by reactions in the Glover tower.

From the Glover tower the gases pass by a lead main to the set of three or more large **lead chambers**, constructed of sheet lead. The chambers are oblong or square in shape and dip into large lead trays with a seal of acid. They are suspended from a wooden or iron frame by lead straps on the sides. All joints in the lead sheets are autogenously welded by a hydrogen flame. Drum-shaped or polygonal ("Mills-Packard") chambers sometimes cooled by water flowing over the outside, or even packed towers, are used in some modern plants, but adequate empty space is necessary for the reoxidation of NO, which is rather slow and hence towers are often combined with chambers.

Steam or more usually a fine spray of liquid water from several jets in the roof is blown into the chamber. Sulphuric acid is produced in the form of a fog of small drops which settle down as liquid *chamber acid* (65-70 per cent. H_2SO_4) on the floor of the chamber.

The gases from the last chamber contain nitrogen, a little oxygen, most of the oxides of nitrogen in circulation through the plant, and a trace of sulphur dioxide. They pass to the **Gay-Lussac tower**, a lined lead tower 40 to 60 ft. high and 8 to 15 ft. diameter, packed with hard coke or pieces of flint and fed with cold Glover acid (78 per cent. H_2SO_4). Its function is to recover the oxides of nitrogen in the exit gases from the chambers. These are absorbed producing *nitrous vitriol* containing nitrososulphuric acid equivalent to 1 to 2 per cent. of N_2O_3 , which is pumped to the Glover tower for denitration. The waste gas from the Gay-Lussac tower passes to a chimney or fan which maintains a draught through the whole system. In modern practice a high concentration of oxides of nitrogen ("circulating nitre") with adequate absorption capacity in the Gay-Lussac towers is used, and the reaction proceeds rapidly but with greater wear of the lead chambers.

Concentration of sulphuric acid.—The acid from the Glover tower contains about 78 per cent. of H_2SO_4 . It is generally dark coloured from contact with organic matter and is called "brown oil of vitriol" (B.O.V.). It is sufficiently concentrated for some commercial purposes, *e.g.* for making superphosphate of lime (p. 342) or saltcake (p. 156), but for others it must be further concentrated to form "rectified oil of vitriol" (R.O.V.) containing 93 to 95 per cent. of H_2SO_4 . This concentration was formerly carried out by heating the acid in glass or platinum retorts, when vapours of weak acid come off and more concentrated acid remains. The concentration is now carried out in special apparatus.

A simple type is the **cascade process**, in which the acid is allowed to flow down a series of silica or ferro-silicon dishes arranged one above the other with the spout of one discharging into the basin next lower, the

whole resting on a kind of staircase of acid-resisting bricks. The acid is heated below and hot air sweeps over its surface by a flue. From the last dish, which may be of cast iron, the acid flows to a cooler.

Another type of apparatus is the **Kessler concentrator**, in which hot furnace gases bubble through a thin layer of acid flowing through a dish of acid-resisting material.

The **Gaillard tower** is an empty tower of Volvic stone or acid-resisting brick, from the top of which a fine spray of acid is discharged. In passing down the tower this spray meets a current of hot gas from a coke furnace which enters the tower at the side near the bottom. The acid is concentrated to 95 per cent. and runs out from a lead tray in which the tower stands, to a cooler.

The strongest sulphuric acid does not attack cast iron whilst 93 to 95 per cent. acid dissolves it. In making 98 per cent. acid the 95 per cent. acid is run in a thin stream on the surface of a large bulk of 98 per cent. acid boiling in a large cast-iron pot. The acid may also be brought to any desired strength by the addition of oleum (sulphuric acid containing free SO_3).

Most of the sulphuric acid is used (as chamber acid) for superphosphate manufacture; next important is the use of concentrated acid for petroleum refining. The rest is used for chemicals, refining coal products, in metallurgical processes, making artificial silk and explosives (when fuming acid is often used), in storage batteries, etc. Some processes which formerly used sulphuric acid (*e.g.* making nitric and hydrochloric acids) are now often carried on without it.

The contact process.—Sulphuric acid and fuming sulphuric acid are now made by the so-called "contact" process (see p. 556), in which sulphur dioxide and oxygen (in the form of air) combine to form sulphur trioxide in presence of a catalyst. The apparatus is very compact as compared with the chamber plant. When platinum is used as a catalyst the gases must be carefully purified, since otherwise the platinum loses its activity or is "poisoned". Arsenious oxide, sulphuric acid fog, and dust in the gases from pyrites burners are removed by introducing steam and cooling, then filtering the gas through coke wetted with concentrated sulphuric acid until no fog is seen by a powerful beam of light ("optically clear" gas).

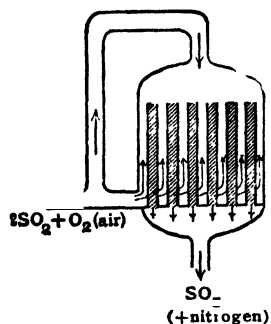


FIG. 234.—Badische converter.

In the **Badische process** the purified gas is passed through an iron converter (Fig. 234) with vertical iron tubes packed with platinised asbestos. Twice the theoretical amount of oxygen (in the form of air) is present in the gas, which is pre-heated to start the reaction. By letting part of the incoming gas sweep over the outside of the hot tubes in which reaction occurs no external

heating is needed, since heat is evolved and the process goes on continuously. In modern plants a preparation of vanadium pentoxide supported on silica granules or platinised silica gel are used as catalysts; they are immune to arsenic poisoning.

The reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3 + 45 \text{ k. cal.}$ is reversible and the law of mass action shows that excess of oxygen favours the production of SO_3 : $[\text{SO}_3]^2/[\text{SO}_2]^2[\text{O}_2] = K$. The equilibrium yield of SO_3 is smaller at higher temperatures, since the reaction is exothermic, (p. 231), but the velocity of reaction is too small at lower temperatures. The conflicting effects of temperature are reconciled by working at the optimum temperature of 400-450° with platinum, and using excess of oxygen in the form of air, when 98 per cent. of the SO_2 is oxidised to SO_3 .

The sulphur trioxide cannot be absorbed from the converter gas by passing through water, as a dense fog of minute droplets of H_2SO_4 is thus formed which cannot be condensed. The gas is therefore passed into concentrated sulphuric acid in iron towers; the concentrated acid rapidly absorbs the SO_3 producing fuming sulphuric acid or *oleum*; or if a regulated stream of water is admitted the 98 per cent. acid is continuously increased in quantity by the reaction $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ occurring in the liquid acid.

Fuming sulphuric acid is an oily liquid which emits thick white fumes in moist air. It may be kept in mild steel drums, but cracks cast iron (which resists the action of ordinary concentrated sulphuric acid). It is made with different contents of free SO_3 , *i.e.* SO_3 in excess of the amount required to form H_2SO_4 . The strongest product contains 60 per cent. of free SO_3 and emits very dense fumes.

Properties of sulphuric acid.—Pure sulphuric acid (*monohydrate*) is prepared by adding the requisite amount of SO_3 to 98 per cent. acid. It is an oily liquid which fumes slightly in air, from dissociation in the liquid:



This dissociation increases on heating and the vapour is richer in SO_3 than the residual liquid. It is therefore impossible to obtain the pure acid by the ordinary concentration process. On boiling, an acid of constant composition (98.3 per cent. H_2SO_4) comes over at a temperature of 338°, which is usually given as the boiling point of sulphuric acid. The 95 per cent. acid boils at 295°. The ordinary acid (98 per cent. H_2SO_4) is a colourless oily liquid of sp. gr. 1.84, which does not fume.

Concentrated sulphuric acid is very corrosive and has a strong affinity for water; when mixed with water much heat is given out and the liquid may boil; the acid should always be added to the water in a thin stream with stirring, never the water to the acid. The diluted acid occupies a smaller volume than its constituents and the contraction is a maximum for $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$. Crystalline compounds $2\text{SO}_3 \cdot \text{H}_2\text{O}$

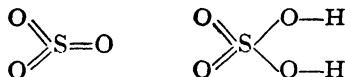
($\text{H}_2\text{S}_2\text{O}_7$), $\text{SO}_3\cdot\text{H}_2\text{O}$ (H_2SO_4), $\text{SO}_3\cdot 3\text{H}_2\text{O}$ and $\text{SO}_3\cdot 5\text{H}_2\text{O}$ are known. If the acid is mixed with snow cold is produced, because the latent heat of fusion of ice exceeds the heat evolved on mixing the acid with liquid water.

On account of its great affinity for water concentrated sulphuric acid is used for drying gases on which it does not act chemically. The affinity of the acid for water is also shown by the charring of organic matter containing carbon, hydrogen and oxygen. The elements of water are removed and black carbon is left.

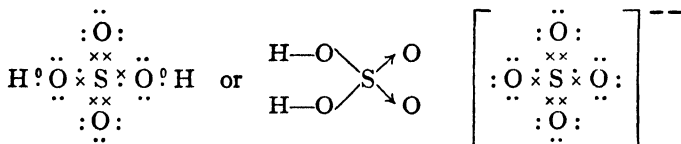
To a strong syrup of cane-sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ contained in a beaker standing in a stoneware trough concentrated sulphuric acid is added. The mixture rapidly becomes dark in colour and hot and froths up into a black mass of finely divided carbon, clouds of steam and sulphur dioxide being evolved.

The vapour density of sulphuric acid is 25, which is the calculated density for complete dissociation into SO_3 and H_2O . The products recombine on cooling: $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_3$. If the vapour is passed through a red-hot platinum or quartz tube the sulphur trioxide is decomposed into oxygen and sulphur dioxide, which do not recombine on cooling: $2\text{H}_2\text{SO}_4 = 2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O}$.

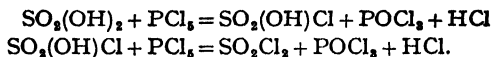
The structural formulae of sulphur trioxide and sulphuric acid are usually written as :



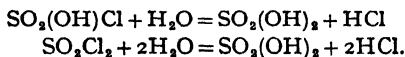
Sulphuric acid and the sulphate ion are represented in electronic formulae (see p. 482) as :



By the action of phosphorus pentachloride on concentrated sulphuric acid one or both hydroxyl groups are replaced by chlorine, forming **chlorosulphonic acid** and **sulphuryl chloride** :

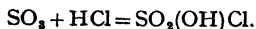


These are liquids decomposed by water into sulphuric and hydrochloric acids :

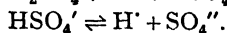
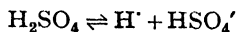


The reaction with chlorosulphonic acid is dangerously violent. Sulphuryl chloride is also formed by the combination of sulphur dioxide and chlorine

and chlorosulphonic acid by the combination of sulphur trioxide and dry hydrogen chloride :



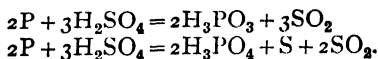
Sulphates.—In aqueous solution sulphuric acid is a strong acid, since it is largely ionised, the second stage only at high dilution :



The acid is dibasic and forms two series of salts MHSO_4 and M_2SO_4 , where M is a univalent metal.

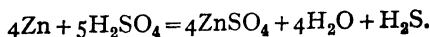
Most sulphates are crystalline and soluble in water : those of lead, calcium and strontium are sparingly soluble ; barium sulphate is practically insoluble in water and dilute acids and its formation is used as a test for sulphuric acid or sulphates. Care should be taken not to add an excess of concentrated hydrochloric or nitric acid, as in that case a white precipitate of barium chloride or nitrate is thrown down, but this readily dissolves in water.

Concentrated sulphuric acid is slowly reduced to sulphur dioxide by hydrogen, especially when heated, by heated carbon, and when boiled with sulphur. Phosphorus decomposes the heated acid with formation of sulphur dioxide and sulphur and the phosphorus is oxidised to phosphorous and phosphoric acids :

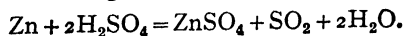


Many metals (Mg, Zn, Fe, etc.) dissolve in *dilute* sulphuric acid with liberation of hydrogen. Sodium, potassium and magnesium liberate hydrogen from the cold *concentrated* acid. Most metals react with the hot concentrated acid with evolution of sulphur dioxide ; iron liberates hydrogen and sulphur dioxide on heating, but the action soon ceases.

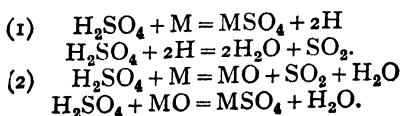
When a mixture of 2 vols. of concentrated sulphuric acid and 1 vol. of water is heated with zinc, hydrogen sulphide is formed and a little sulphur is deposited :



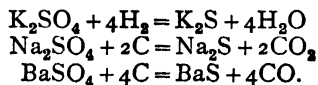
The hot concentrated acid gives sulphur dioxide :



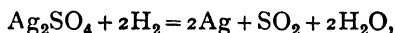
The reduction of hot concentrated sulphuric acid to sulphur dioxide by metals has been represented by two sets of equations in which M is a bivalent metal :



Alkali metal (except ammonium) sulphates and those of lead and magnesium are stable on heating, except at very high temperatures; sulphates of zinc, copper, and iron at high temperatures evolve SO_3 , SO_2 and oxygen; calcium sulphate is decomposed at a high temperature but strontium and barium sulphates are stable. Most sulphates are reduced to sulphides by heating in a current of hydrogen or with carbon:



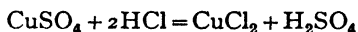
Silver sulphate is reduced by hydrogen to the metal:



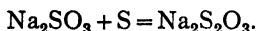
and aluminium and chromium sulphates form the oxides:



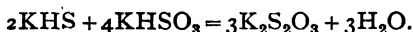
Copper sulphate is decomposed when heated in a current of hydrogen chloride:



Sodium thiosulphate.—On boiling powdered sulphur with sodium sulphite solution in a flask, sodium thiosulphate is formed:



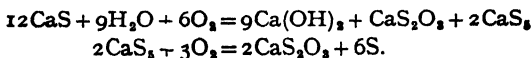
On evaporating the filtered solution and cooling, the hydrated salt $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ separates in crystals, used in photography and commonly called sodium "hyposulphite" (or "hypo"). Pure sodium thiosulphate and especially potassium thiosulphate ($3\text{K}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) are best prepared by the reaction of alkali hydrogen sulphides and hydrogen sulphites in solution and crystallising:



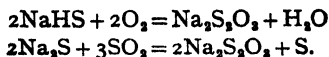
The structural formula of thiosulphuric acid (p. 556) is: $\text{SO}_2 \begin{matrix} \nearrow \text{OH} \\ \searrow \text{SH} \end{matrix}$

Sodium thiosulphate was formerly made by oxidising alkali waste containing calcium sulphide by exposure to air, and then precipitating the calcium thiosulphate solution formed with sodium carbonate.

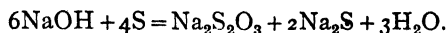
When a solution of a sulphide is exposed to air a complicated series of reactions occurs. Polysulphides, free sulphur, thiosulphate and sulphate may all be formed according to the conditions of the reaction:



Sodium thiosulphate is formed by the action of oxygen or sulphur dioxide on heated sulphides:



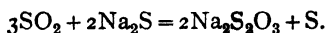
If sulphur is boiled with an alkali hydroxide solution or milk of lime, a thiosulphate is produced as well as a sulphide or polysulphide :



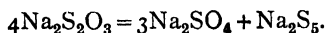
When sulphur is fused with alkali (or carbonate) the same reaction occurs but the thiosulphate is mostly decomposed into sulphate and sulphide (see below). Liver of sulphur (*hepar sulphuris*) is a dark-brown mass formed by fusing potassium carbonate with sulphur and contains potassium sulphides and sulphate :



Thiosulphates are also formed by passing sulphur dioxide into solutions of sulphides :



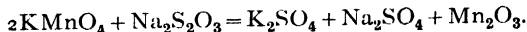
Sodium thiosulphate crystals on heating melt and lose water and above 220° decompose (at higher temperatures Na_2S_5 loses sulphur) :



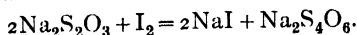
On acidifying a solution of sodium thiosulphate free thiosulphuric acid is perhaps formed but decomposes into sulphurous acid and sulphur : $\text{H}_2\text{S}_2\text{O}_3 = \text{H}_2\text{SO}_3 + \text{S}$. A solution of the acid is formed by the action of a solution of HCl in ether on sodium thiosulphate at -78° . Above -5° it decomposes : $\text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{S} + \text{SO}_3$.

Sodium thiosulphate readily dissolves silver chloride, bromide and iodide forming a double sodium silver thiosulphate. For this reason the salt is used in photography (pp. 324, 327).

Thiosulphates are readily oxidised by chlorine or bromine water : tetrathionate, sulphate, and some trithionate ($\text{Na}_2\text{S}_3\text{O}_6$) are formed and sulphur is precipitated. With a large excess of halogen some sulphur is slowly oxidised to sulphuric acid (p. 164). Sodium thiosulphate is used as an *antichlor* to remove traces of chlorine from bleached fabrics. Potassium permanganate in *neutral* solution oxidises thiosulphate to sulphate (in *acid* solution some dithionate $\text{Na}_2\text{S}_2\text{O}_6$ is also formed) :



On adding a solution of sodium thiosulphate to a solution of iodine in potassium iodide the brown colour of the iodine is discharged and **sodium tetrathionate**, discovered by Fordos and Gélis in 1843, is formed. The reaction is quantitative :



To obtain the pure salt a saturated aqueous solution of sodium thiosulphate is added drop by drop to a cooled solution of iodine in alcohol, with shaking after each addition, until only a pale yellow colour remains. The tetrathionate separates in crystals; it is washed with alcohol, dissolved

in water, reprecipitated with alcohol and dried in a desiccator over sulphuric acid. In solution the salt slowly decomposes:



Persulphuric acids.—Faraday in 1834 when electrolysing a concentrated solution of sulphuric acid observed that “a remarkable disappearance of oxygen took place”, but thought this was due to the formation of hydrogen peroxide. In 1878 Berthelot exposed a mixture of sulphur dioxide and oxygen to the silent discharge and obtained long prismatic crystals supposed to be **persulphuric anhydride** S_2O_7 . Marshall in 1890 found that on electrolysis of a concentrated solution of potassium hydrogen sulphate crystals of **potassium persulphate** $\text{K}_2\text{S}_2\text{O}_8$ separate at the anode.

Persulphuric acid (or *perdisulphuric acid*) is formed by the electrolysis of 50 per cent. sulphuric acid with an anode of platinum wire surrounded by a

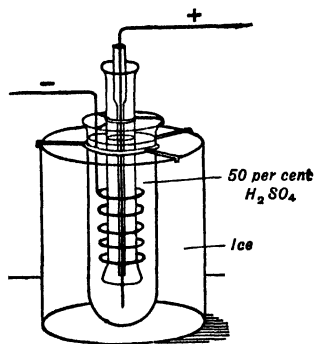
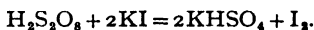
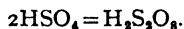


FIG. 235.—Preparation of persulphuric acid.

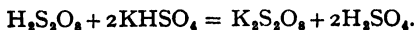
glass tube to serve as a diaphragm. The cathode is a spiral of copper wire outside the diaphragm (Fig. 235). The apparatus is immersed in ice. If a saturated potassium hydrogen sulphate solution is used crystals of the persulphate separate out. The solution in each experiment gives a brown colour with potassium iodide:



In the preparation of potassium persulphate the ions HSO_4' are discharged and persulphuric acid is formed:

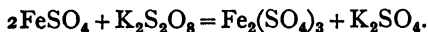


This reacts with the potassium hydrogen sulphate, and the sparingly soluble persulphate crystallises out:

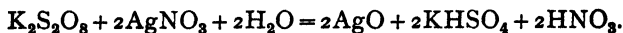


The ammonium salt $(\text{NH}_4)_2\text{S}_2\text{O}_8$, prepared in a similar way to the potassium salt, is the most soluble persulphate.

Persulphates are powerful oxidising agents, slowly liberating iodine from iodides, and oxidising ferrous to ferric salts:

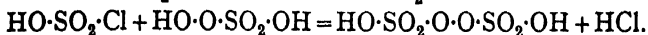
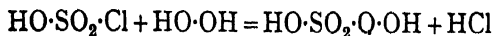


Potassium (but not ammonium) persulphate precipitates black argentic oxide $\text{Ag}^{\text{II}}\text{O}$ from silver nitrate solution:



By the action of concentrated sulphuric acid on potassium persulphate another persulphuric acid H_2SO_5 (**permonosulphuric acid** or *Caro's acid*) is formed, which at once liberates iodine from potassium iodide. Both

persulphuric acids can be obtained as pure solids by the action of anhydrous hydrogen peroxide on chlorosulphonic acid :



They are substitution products of hydrogen peroxide, $\text{H}\cdot\text{O}\cdot\text{O}\cdot\text{H}$, and are used in its manufacture (p. 142).

The atomic weight of sulphur was determined from the synthesis of silver sulphide and the analysis of silver sulphate. Richards and Jones determined the ratio $\text{Ag}_2\text{SO}_4 : 2\text{AgCl}$ and Richards and Hoover the ratio $\text{Na}_2\text{CO}_3 : \text{Na}_2\text{SO}_4$. These results involve the atomic weights of other elements (silver and carbon) and more direct and perhaps more accurate values have been found from the limiting densities of hydrogen sulphide and sulphur dioxide by Baume and Perrot (1908).

The valency follows from the atomic heat (which is rather low, 5.6) and the densities of several gaseous or volatile compounds.

CHAPTER XXXI

CHROMIUM

History.—A red Siberian mineral now called *crocoisite* was described by J. G. Lehmann in 1766; in 1797 Vauquelin and Klaproth found that it was lead chromate PbCrO_4 , containing the new element chromium. The name chromium (Greek, *chroma* = colour) was given to the element because it forms a large number of coloured compounds. Metallic chromium was obtained by Vauquelin by reducing the sesquioxide Cr_2O_3 with carbon at a white heat.

Occurrence.—Chromium occurs in small amounts in some iron meteorites. The commonest ore is *chromite* or *chrome-ironstone*, which is ferrous chromite FeCr_2O_4 or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, a spinel (p. 377). Rarer minerals are *chrome-ochre* Cr_2O_3 and *chromitite* $\text{Fe}_2\text{O}_3 \cdot 2\text{Cr}_2\text{O}_3$.

Chromite is mined principally in Greece, Asia Minor, India, Rhodesia and New Caledonia. It is very refractory and is made into chrome bricks for furnace linings or to separate the silica bricks from the magnesia bricks in the lining of the basic hearth steel furnace. Chromite is the source of chromium compounds.

Chromium forms three series of compounds :

- (i) the **chromous salts** containing 2-valent Cr ;
- (ii) the **chromic salts** containing 3-valent Cr ;
- (iii) the **chromates** (and dichromates) containing 6-valent Cr.

Metallic chromium.—Chromium is obtained by reducing the green sesquioxide in perfectly dry hydrogen at 1500° or with aluminium in the *Thermit process* (p. 374) : $\text{Cr}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Cr}$.

A tin canister 10 in. by 6 in. is filled with coarsely powdered fluorspar and a depression 2 in. \times 8 in. made in it by a large test-tube. The mixture of the dry oxide and aluminium powder is pressed into this and the $(\text{BaO}_3 + \text{Mg})$ igniter placed on the top (Fig. 236). The fluorspar is a good heat insulator so that a fused mass is obtained even with small amounts of material. A mixture of aluminium powder with an equal or

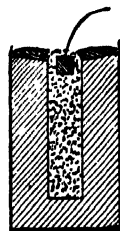


FIG. 236.—Arrangement for Thermit reaction.

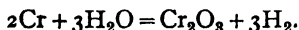
double weight of calcium turnings, corresponding with the oxygen of the oxide, acts even more effectively than aluminium alone and is used in the case of difficultly reducible oxides such as Cr_2O_3 ; or a mixture of 4 pts. Cr_2O_3 , 1 pt. powdered fused $\text{K}_2\text{Cr}_2\text{O}_7$, and 1.9 pts. Al powder, is used.

Pure chromium is obtained by electrolysing a solution of chromic chloride CrCl_3 with a mercury cathode and heating the amalgam in a vacuum to remove mercury. It is also deposited electrolytically in chromium plating (see below).

An alloy of iron and chromium called *ferrochrome* is made industrially by reducing chrome ironstone with carbon in the electric furnace and is used in the manufacture of *chrome steel* (steel containing chromium).

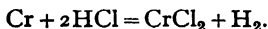
Chrome steel is not attacked by acids. An alloy of chromium, nickel and iron is used for armour-plates. *Stainless steel* is ordinary steel with 12 to 14 per cent. of chromium and up to 0.7 per cent. of nickel. Steels with 17 to 18 per cent. of chromium and 7 per cent. or more of nickel are not hardened by quenching and have superior corrosion resistance.

Chromium is a hard crystalline but malleable metal, silver-white with a bluish tinge, with a high melting point. It burns brilliantly in the oxyhydrogen flame forming the sesquioxide Cr_2O_3 , and decomposes steam at a red heat :

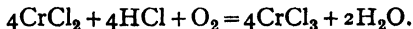


The finely divided chromium left on heating the amalgam is pyrophoric ; it combines with nitrogen on heating forming the *nitride* CrN .

Chromium dissolves slowly in dilute sulphuric and hydrochloric acids especially on heating, forming blue solutions of **chromous salts** :



The solutions rapidly absorb atmospheric oxygen, forming green solutions of **chromic salts** :



Hot concentrated sulphuric acid attacks chromium rapidly, sulphur dioxide being evolved. Dilute nitric acid also dissolves it but in the concentrated acid it becomes *passive* and is then unattacked by dilute acids. Passivity (perhaps due to a film of oxide) is also induced by exposure to air or dipping in chromic acid. It is destroyed by touching the metal under the surface of dilute sulphuric acid with zinc.

Chromium is deposited (usually on nickel) in *chromium plating* from a hot solution of chromic acid and a little chromic sulphate with a lead anode.

CHROMOUS SALTS

The chromous salts contain 2-valent chromium and are powerful reducing agents. They are formed by dissolving the metal in acids or by reducing chromic salts with nascent hydrogen (zinc and dilute acid) :

$\text{Cr}''' + \text{H} = \text{Cr}'' + \text{H}'$. This reaction is reversible and chromous salts in acid solution evolve hydrogen, especially in contact with platinum.

50 gm. of pure granulated zinc and 10 gm. of finely powdered potassium dichromate are placed in a flask fitted with a tap-funnel and a delivery tube dipping under water (Fig. 237). 200 c.c. of concentrated hydrochloric acid mixed with 100 c.c. of water are added. A violent reaction occurs, the liquid first becoming green (CrCl_3) and then blue (CrCl_2). The liquid is rapidly passed through an asbestos filter into a saturated solution of sodium acetate (92 gm. of sodium acetate crystals), when red chromous acetate $\text{Cr}(\text{CH}_3\text{CO}_2)_2$ is thrown down. This is fairly stable; it is washed in a closed flask by decantation with water saturated with carbon dioxide.

The second part of the preparation is more difficult. The air is expelled from the flask by hydrogen and the solid dissolved in concentrated hydrochloric acid. A blue solution of chromous chloride is formed. This is cooled in ice and a current of hydrogen chloride gas passed through. Chromous chloride $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ is precipitated in blue needles.

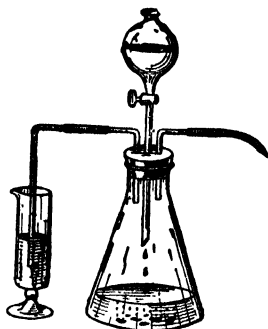


FIG. 237.—Preparation of chromous chloride.

Anhydrous chromous chloride is obtained by heating chromic chloride in hydrogen: $2\text{CrCl}_3 + \text{H}_2 = 2\text{CrCl}_2 + 2\text{HCl}$, or metallic chromium in hydrogen chloride. It forms *white* silky needles. The vapour density at high temperatures corresponds with the equilibrium: $\text{Cr}_2\text{Cl}_4 \rightleftharpoons 2\text{CrCl}_2$.

Caustic soda added to a solution of a chromous salt in absence of air precipitates brownish-yellow chromous hydroxide $\text{Cr}(\text{OH})_2$, which is readily oxidised in air and in the moist state evolves hydrogen: $2\text{Cr}(\text{OH})_2 + 2\text{H}_2\text{O} = 2\text{Cr}(\text{OH})_3 + \text{H}_2$. Chromous oxide CrO cannot therefore be obtained by heating the hydroxide; it is said to be formed as a black powder on exposure of chromium amalgam to air.

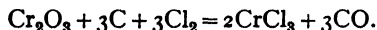
Chromous sulphate $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ is obtained in fine blue crystals isomorphous with ferrous sulphate by dissolving the acetate or metal in dilute sulphuric acid and cooling the solution. It forms double salts, e.g. $\text{K}_2\text{SO}_4 \cdot \text{CrSO}_4 \cdot 6\text{H}_2\text{O}$. The ammoniacal solution of CrSO_4 absorbs acetylene and the aqueous solution absorbs oxygen and nitric oxide.

CHROMIC SALTS

The chromic salts are stable compounds containing 3-valent chromium and mostly exist in at least two modifications: (i) a *violet* form in hydrated crystals or in solution, the latter containing the chromic ion Cr''' or probably $[\text{Cr}(\text{H}_2\text{O})_6]'''$; and (ii) one or more *green* modifications in which

part or all of the chromium is present as a complex ion. In the green solutions there is generally hydrolysis. With very weak acids 3-valent chromium forms complex salts in which it exists in very stable *anions*. Another group of complex compounds are the *ammine* compounds with ammonia, *e.g.* $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$.

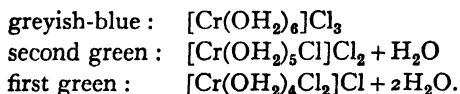
Anhydrous **chromic chloride** is obtained as a sublimate of peach-blossom coloured scaly crystals when chlorine is passed over chromium or a mixture of chromium sesquioxide and carbon heated to redness :



The vapour density corresponds with CrCl_3 . The crystals are almost insoluble in cold water and are not attacked by boiling concentrated sulphuric acid, but readily dissolve in water in presence of a trace of chromous chloride (or a reducing agent such as SnCl_2 or CuCl) giving a green solution.

Three crystalline hydrates $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are known, all readily soluble in water, viz. two *green* and one *greyish-blue*. The first green chloride is the common form. It is obtained by dissolving chromic hydroxide in hydrochloric acid or when chromic anhydride is boiled with concentrated hydrochloric acid until all the chlorine has been given off : $2\text{CrO}_3 + 12\text{HCl} = 2\text{CrCl}_3 + 3\text{Cl}_2 + 6\text{H}_2\text{O}$. The solution is then evaporated until its weight corresponds with less water than $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, then made up to this weight and cooled. The other two forms are prepared from the common green form by suitable treatment with hydrochloric acid.

In solution the greyish-blue chloride gives three chloride ions, since all the chlorine can be precipitated with silver nitrate. The second green form gives only two chloride ions and readily loses a molecule of water. The first green form gives only one chloride ion and readily loses two molecules of water. Werner represented the constitution of the three forms as follows :

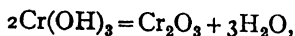


The atoms or molecules inside the square brackets are directly co-ordinated (p. 265) with the metal atom and are not ionisable, whereas the radicals outside are ionisable. The number of atoms or molecules co-ordinated with the chromium atom is always six.

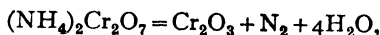
Chromic nitrate $\text{Cr}(\text{NO}_3)_3$ is obtained by dissolving the hydroxide in nitric acid and crystallising with $9\text{H}_2\text{O}$. It is stable in the violet form and its solution only very slowly becomes green on heating, recovering the violet colour on cooling. The chloride and sulphate, on the other hand,

readily form green solutions on heating and these pass into the violet form only on long standing in the cold. If the acid formed by hydrolysis is nearly neutralised by alkali, and then an acid is added, a violet solution is rapidly formed.

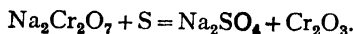
Chromic oxide (or *chromium sesquioxide*) is produced as a green powder insoluble in water by heating chromic hydroxide :



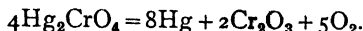
or ammonium dichromate :



or sodium dichromate with sulphur in an iron pot and washing out the sodium sulphate from the residue :



A very fine green oxide is produced by gently heating mercurous chromate :



Dark-green hard hexagonal crystals are formed by fusing the amorphous oxide with calcium carbonate and boron trioxide, by igniting a mixture of potassium dichromate and common salt, or by passing the vapour of chromyl chloride CrO_2Cl_2 through a red-hot tube.

The oxide produced by ignition of the hydroxide or ammonium dichromate is insoluble in acids except hot 70 per cent. perchloric acid which oxidises it to CrO_3 ; it may be brought into solution by fusing with potassium hydrogen sulphate or sodium peroxide, or by heating with alkaline permanganate when a chromate is formed with deposition of manganese dioxide.

Chromic oxide has a very high melting point and is very refractory, but it dissolves in fused borax or glass, giving a green colour which becomes blue if strontium is present; this is applied in tinting glass and painting porcelain. The oxide is used as a permanent green oil paint under the name of *chrome-green*.

Chromic hydroxide is formed as a pale greyish-green flocculent precipitate by adding alkali hydroxide or ammonia to a solution of a chromic salt. On standing in contact with a dilute alkali the precipitate slowly "ages" and changes its properties. By precipitating a cold solution of a violet chromic salt with ammonia, a pale-blue precipitate is formed which readily dissolves in sodium hydroxide solution to a grass-green solution which may contain a chromite $\text{Na}_2\text{Cr}_2\text{O}_4$. Natural chrome-ironstone is ferrous chromite FeCr_2O_4 . All the chromium hydroxide is deposited from the green solution on boiling. A dark-green colloidal solution is obtained by dialysing a solution of the freshly precipitated hydroxide in chromic

chloride solution. It can be boiled but is coagulated by salts. Chromium hydroxide, like aluminium hydroxide, is appreciably soluble in *concentrated* ammonia.

By fusing together equimolecular amounts of potassium dichromate and crystallised boric acid and lixiviating with water, a brilliant green powder used as a pigment under the name of *Guignet's green* is left. This is usually supposed to be the hydroxide $\text{Cr}_2\text{O}(\text{OH})_4$.

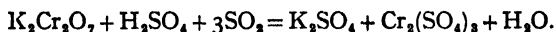
Chromic sulphide Cr_2S_3 is obtained by heating sulphur with chromium or CrCl_3 in H_2S . By adding a solution of ammonium sulphide to a chromic salt the hydroxide is precipitated, as the sulphide is completely hydrolysed by water: $2\text{CrCl}_3 + 6\text{H}_2\text{O} + 3(\text{NH}_4)_2\text{S} = 2\text{Cr}(\text{OH})_3 + 6\text{NH}_4\text{Cl} + 3\text{H}_2\text{S}$.

Chromic sulphate is obtained in bluish-violet crystals by allowing a mixture of equal parts of concentrated sulphuric acid and chromic hydroxide (dried at 100°) to stand for some weeks in a loosely-stoppered bottle. If its solution is precipitated with a little alcohol violet octahedra of $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ are deposited.

By heating potassium dichromate or chrome alum with concentrated sulphuric acid an olive-coloured acid sulphate $2\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ completely insoluble in water and acids is formed.

Chromic sulphate forms alums with sulphates of the alkali metals. **Potassium chromic sulphate** or ordinary **chrome alum** has the formula $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ or $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. It is obtained by reducing a solution of potassium dichromate acidified with sulphuric acid, and forms dark-purple octahedral crystals. Chrome alum is used in dyeing and calico-printing and in tanning. The following experiment is a convenient method of preparation:

Dissolve 20 gm. of potassium dichromate in 150 c.c. of hot water and after cooling add 4 c.c. of concentrated sulphuric acid. Pass sulphur dioxide carefully into the *well-cooled* solution until the red colour, which at first changes to brown and then to olive-green, has become green-blue:

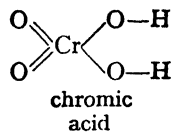
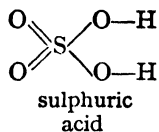
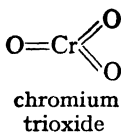
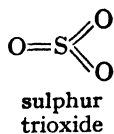


Set aside in a covered dish for some time and observe the formation of purple octahedral crystals of chrome alum. Instead of sulphur dioxide, alcohol may be used in the reduction and is oxidised to aldehyde.

A solution of chrome alum in cold water has a dull bluish-red colour; on heating to 70° it becomes green. Barium chloride precipitates the sulphate in the violet solution completely whilst the green solution is not completely precipitated. If the green solution is allowed to stand for some time in the cold it becomes violet.

CHROMIUM TRIOXIDE AND THE CHROMATES

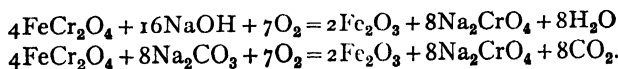
The acidic trioxide CrO_3 contains 6-valent chromium and forms salts derived from a **chromic acid** H_2CrO_4 which is not known but is analogous to sulphuric acid :



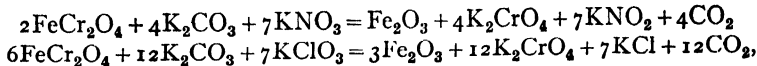
Chromic acid forms **normal chromates** (e.g. K_2CrO_4) and **dichromates** (e.g. $\text{K}_2\text{Cr}_2\text{O}_7$), analogous to sulphates and disulphates.* Acid chromates, e.g. KHCrO_4 are not known but by the action of excess of CrO_3 or by boiling the dichromate with nitric acid, **trichromates** (e.g. $\text{K}_2\text{Cr}_3\text{O}_{10}$ or $\text{K}_2\text{O}_3\text{CrO}_3$) and **tetrachromates** (e.g. $\text{K}_2\text{Cr}_4\text{O}_{13}$ or $\text{K}_2\text{O}_4\text{CrO}_3$) are formed as red crystals.

Manufacture of chromates and dichromates.—In the manufacture of chromates and dichromates the starting material is the mineral *chromite* or *chrome ironstone* FeCr_2O_4 (ferrous chromite).

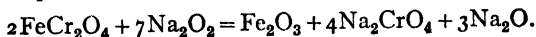
When finely powdered chromite is strongly heated with an alkali or alkali carbonate with free exposure to air, the chromium is slowly oxidised to a soluble chromate and the ferrous iron to ferric oxide :



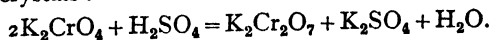
Oxidation is more rapid with a mixture of alkali carbonate and potassium nitrate or chlorate :



or with sodium peroxide :



On the technical scale fusion with potassium carbonate was formerly used, the yellow solution of potassium chromate being acidified with sulphuric acid when **potassium dichromate** $\text{K}_2\text{Cr}_2\text{O}_7$ is formed on cooling in bright red crystals :



In the modern process a mixture of finely powdered chromite, sodium carbonate and quicklime is heated to redness on the hearth of a reverberatory furnace with free exposure to air, when all the carbon dioxide is

* A common mistake is to suppose that a dichromate is formed by "oxidising" a chromate (as a permanganate is formed by oxidising a manganate). Both chromate and dichromate contain the same 6-valent chromium.

expelled and sodium chromate is produced. The function of the quicklime is probably to keep the mass porous and prevent fusion. The sodium chromate is extracted with water and concentrated sulphuric acid is added :

$$2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}.$$

The sodium sulphate separates and is removed. The solution is concentrated and deliquescent red crystals of sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ slowly separate on cooling.

The sodium salt is much cheaper and more soluble, but may be converted into potassium dichromate by potassium chloride in solution. Chromates and dichromates are used as oxidising agents, as mordants in dyeing and in preparing insoluble pigments.

Chromium trioxide.—By the action of concentrated sulphuric acid on a solution of a chromate or dichromate, red chromium trioxide CrO_3 is obtained. This is often called "chromic acid" although it is the anhydride of this acid, which would have the formula H_2CrO_4 . The aqueous solution of chromium trioxide has a red colour and is strongly acid. The colour, the depression of freezing point and the conductivity show that the substance is mostly present as **dichromic acid** $\text{H}_2\text{Cr}_2\text{O}_7$ or the ion $\text{Cr}_2\text{O}_7^{--}$:

$$2\text{CrO}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + \text{Cr}_2\text{O}_7^{--}.$$

Chromium trioxide is prepared in the laboratory as follows :

Dissolve 50 gm. of $\text{K}_2\text{Cr}_2\text{O}_7$ in 85 c.c. of hot water and to the cooled solution add slowly with stirring 70 c.c. of concentrated H_2SO_4 . Allow to stand for twelve hours and pour the liquid off the crystals of acid potassium sulphate which have separated :

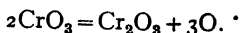


Heat to 85° , add 25 c.c. of sulphuric acid and sufficient water just to dissolve the CrO_3 , separating. Allow to stand twelve hours and decant the liquid from the crystals of CrO_3 . Wash the latter with pure nitric acid in a Buchner funnel containing asbestos, drain well and heat to 60° to 80° in a current of pure dry air in a tube to remove adhering nitric acid.

The pure chromium trioxide so prepared forms small needle-shaped crystals of a bright violet-red colour. Chromium trioxide is very deliquescent. It melts when heated to a dark red liquid, solidifying on cooling to a reddish-black mass with a metallic lustre. When more strongly heated it loses oxygen : $4\text{CrO}_3 = 2\text{Cr}_2\text{O}_3 + 3\text{O}_2$, and a little of the trioxide sublimes. **Chromium dioxide** CrO_2 is said to be formed as an intermediate stage, or by heating chromic nitrate, but it has a somewhat variable composition.

Chromium trioxide is a *very powerful oxidising agent*. Alcohol dropped on it catches fire and the concentrated solution is reduced by sugar, oxalic acid, paper, cork, etc. It oxidises sulphur dioxide, hydrogen sulphide,

stannous chloride, arsenious oxide, ferrous salts, etc. In acid solutions the reduction always proceeds to the stage of a chromic salt :



A solution of potassium dichromate mixed with sulphuric acid is very often used as an oxidising agent ; a solution of chromium trioxide in glacial acetic acid (which is not oxidised) is also used.

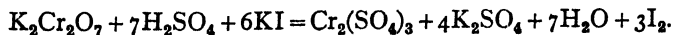
Chromates.—Metallic chromates if soluble are formed from the oxides or carbonates and chromic acid ; they are often insoluble and can then be prepared by double decomposition. All soluble chromates are poisonous.

Potassium chromate K_2CrO_4 is obtained in lemon-yellow readily soluble crystals by evaporating a solution prepared by adding the correct amount of potassium hydroxide to a solution of chromic acid or potassium dichromate. The salt is isomorphous with potassium sulphate. Its yellow solution is alkaline.

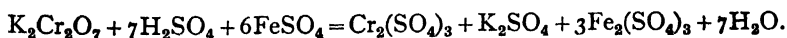
Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ may be obtained by adding the requisite amount of sulphuric acid to a saturated solution of the normal chromate, and crystallises out on cooling in garnet-red crystals. It is much less soluble than the normal chromate and forms a red solution.

Both potassium salts are non-deliquescent and crystallise without water. **Sodium chromate** $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ and **dichromate** $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, made on a large scale, are deliquescent. **Ammonium chromate** $(\text{NH}_4)_2\text{CrO}_4$ is unstable and tends to lose ammonia, forming the dichromate ; it is obtained by crystallising solutions containing excess of ammonia. **Ammonium dichromate** $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is readily obtained by adding ammonia to the requisite amount of chromium trioxide in solution and crystallising. It forms orange-red crystals which decompose violently on heating, evolving nitrogen and steam and leaving a voluminous dull-green mass of chromic oxide (p. 465).

Potassium dichromate in acid solution liberates iodine from potassium iodide :



It is used in volumetric analysis for the estimation of ferrous iron. In acting as an oxidising agent it is reduced to a chromic salt :



The most important sparingly soluble chromates are :

Silver chromate Ag_2CrO_4 ; brick-red, rather difficultly soluble in acids and ammonia.

Barium chromate BaCrO_4 ; yellow, insoluble in acetic acid, soluble in hydrochloric, nitric and chromic acids.

Zinc chromate (basic) $\text{Zn}_3(\text{OH})_2\text{CrO}_4 \cdot \text{H}_2\text{O}$; a yellow pigment.

Lead chromate PbCrO_4 (*chrome-yellow*—used as a pigment)—precipitated from $\text{Pb}(\text{NO}_3)_2$ and $\text{K}_2\text{Cr}_2\text{O}_7$; soluble in nitric acid and in caustic potash.

Basic lead chromate Pb_2CrO_5 (*chrome-red*—used as a pigment)—by digesting PbCrO_4 with cold caustic soda; mixed with PbCrO_4 it forms the pigment *chrome-orange*.

Basic bismuth dichromate $(\text{BiO})_2\text{Cr}_2\text{O}_7$; orange yellow.

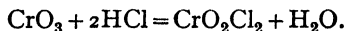
Chromyl chloride.—Sulphuryl chloride SO_2Cl_2 is the chloride of sulphuric acid $\text{SO}_2(\text{OH})_2$, and chromyl chloride CrO_2Cl_2 is the chloride of the *hypothetical* chromic acid $\text{CrO}_2(\text{OH})_2$ or H_2CrO_4 :



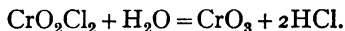
Chromyl chloride is prepared by distilling a mixture (best previously fused together) of sodium chloride and potassium dichromate in a retort with concentrated sulphuric acid; a deep red vapour of chromyl chloride is produced which condenses in a cooled receiver to a deep red (nearly black) liquid like bromine:



If concentrated sulphuric acid is added in small quantities at a time to a cooled solution of chromium trioxide in concentrated hydrochloric acid, chromyl chloride separates and may then be distilled:

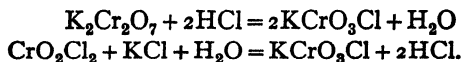


Chromyl chloride has the normal vapour density. It is violently decomposed by water:



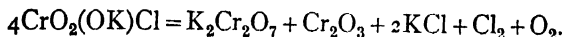
Chromyl chloride is a powerful oxidising agent, exploding in contact with phosphorus (*cf.* Br_2) and inflaming sulphur, ammonia, alcohol and many organic substances. Bromides and iodides do not produce corresponding compounds when distilled with dichromate and sulphuric acid but the free halogen is liberated: this may be utilised in the detection of chlorides in presence of bromides and iodides, since if a chloride is present the distillate when collected in water produces chromic acid and gives with lead salts a yellow precipitate of PbCrO_4 .

When three parts of powdered potassium dichromate are dissolved in four parts of warm concentrated hydrochloric acid and a little water and the liquid cooled, or if chromyl chloride is added to a saturated solution of potassium chloride, red crystals of **potassium chlorochromate** KCrO_3Cl are formed:

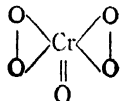


This is known after its discoverer as *Peligo's salt* (1833); it probably has the constitution $\text{Cl}.\text{CrO}_2.\text{OK}$ and is the salt of an unknown chlorochromic acid $\text{CrO}_2(\text{OH})\text{Cl}$, corresponding with chlorosulphonic acid $\text{SO}_2(\text{OH})\text{Cl}$.

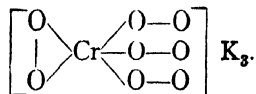
Peligo's salt is partly decomposed by water and decomposes on heating with evolution of chlorine and oxygen:



Perchromic acid is the name given to the deep blue substance formed by the action of hydrogen peroxide on chromic acid (p. 145). Although previously formulated as $\text{CrO}_3.\text{H}_2\text{O}_2$ or H_2CrO_5 , it appears to be an oxide of 6-valent chromium having the formula CrO_5 and the structure:



From chromates and hydrogen peroxide in *alkaline* solution red perchromates, *e.g.* K_3CrO_5 , containing 5-valent chromium are obtained:



The atomic weight of chromium has been found by reducing silver chromate and dichromate with sulphurous acid and precipitating the silver as chloride or bromide. The valency is found from the atomic heat, the vapour density of CrCl_3 and CrO_2Cl_2 , and the isomorphism of chromates and sulphates.

CHAPTER XXXII

MANGANESE

SUB-GROUP (a) of Group VII contains manganese and the rare metal rhenium; sub-group (b) contains the halogen elements. The only property in which manganese shows analogies with the halogen elements is the formation of a higher acidic oxide Mn_2O_7 , which forms permanganates, e.g. KMnO_4 , isomorphous with perchlorates, e.g. KClO_4 . The oxide Mn_2O_7 is also volatile and explosive like Cl_2O_7 . Both silver perchlorate and silver permanganate are sparingly soluble in water.

In its remaining compounds manganese shows close analogies with chromium and iron, the two elements of adjoining groups in the same period. The metals are similar in physical properties and both manganese and chromium form basic sesquioxides and salts of acidic trioxides. Potassium chromate (yellow) K_2CrO_4 and potassium manganate (green) K_2MnO_4 are isomorphous. The salts corresponding with the sesquioxide Mn_2O_3 , e.g. $\text{Mn}_2(\text{SO}_4)_3$, are much less stable than those of chromium, e.g. $\text{Cr}_2(\text{SO}_4)_3$. Manganese resembles iron in forming three oxides of the types MO , M_2O_3 , and M_3O_4 , the first two of which form series of salts. The manganous salts, however, are more stable than the ferrous salts, e.g. they do not undergo oxidation on exposure to air. Manganese resembles magnesium in forming a sparingly soluble compound MnNH_4PO_4 .

History.—The most important ore of manganese is the black dioxide MnO_2 , *pyrolusite*, referred to by Pliny as *magnes* but confused with the magnetic oxide of iron Fe_3O_4 . The name *pyrolusite* (Greek *pyr* fire, *luo* I wash) refers to the use of the mineral in decolorising green glass. If pyrolusite is added in small quantity the green ferrous silicate is oxidised to ferric silicate which has a pale yellow colour, neutralised by the purple tinge imparted by the manganese. With excess of pyrolusite a violet colour is produced.

Metallic manganese was first obtained in an impure form by Gahn by strongly heating the oxide with carbon: $\text{MnO}_2 + 2\text{C} = \text{Mn} + 2\text{CO}$.

Occurrence.—Pyrolusite occurs in the Caucasus, Spain, India and Brazil. It is usually contaminated with ferric oxide and barium, often in the form of *psilomelane* $(\text{Mn}, \text{Ba})\text{O} \cdot 2\text{MnO}_2$, corresponding with Weldon

mud $\text{CaO}, 2\text{MnO}_2$. Pyrolusite always contains less oxygen than corresponds with the formula MnO_2 . Most of the ore is now used in smelting for ferromanganese.

Less important minerals are *braunite* Mn_2O_3 , *hausmannite* Mn_3O_4 , *manganite* $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$, hydrated dioxides *wad* and *psilomelane*, *diatagite* or *rhodocrosite* MnCO_3 , *rhodonite* MnSiO_3 , and the sulphides *alabandite* MnS and *hauerite* MnS_2 . The deposits of hydrated oxides are sedimentary (precipitates, or derived from oxidation by plants etc. in lakes) or metamorphic (derived from the weathering of rocks).

Metallic manganese.—Impure manganese is obtained by reducing the oxides with carbon at a high temperature. If less than the theoretical amount of carbon is used and the mixture heated in the electric furnace, a purer metal (nearly free from carbon) is produced : $\text{MnO} + \text{C} = \text{Mn} + \text{CO}$. A purer metal is obtained by heating the chloride with sodium or magnesium or by reducing the oxide Mn_2O_3 with aluminium in the Thermit process (p. 571) : $3\text{Mn}_2\text{O}_3 + 8\text{Al} = 9\text{Mn} + 4\text{Al}_2\text{O}_3$. The purest metal is obtained by electrolysis of a concentrated solution of manganous chloride with a mercury cathode and distilling off the mercury in a vacuum.

Manganese is a greyish-white, or reddish-white, hard and brittle metal of high melting point. When pure it is not easily oxidised by air. The metal unless very pure decomposes water even in the cold with evolution of hydrogen and readily dissolves in dilute acids forming manganous salts : $\text{Mn} + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{H}_2$. It unites directly with nitrogen at a high temperature forming nitrides Mn_5N_2 and Mn_3N_2 (also formed by passing ammonia over the heated metal), and with carbon in the electric furnace forming a soft carbide Mn_3C .

Alloys of iron and manganese are *ferromanganese* and *spiegeleisen* (so-called from its flat mirror-like crystals; it also contains carbon); *manganese steel* is very hard and tough and is used for machinery. *Manganese bronze* is copper alloyed with manganese and zinc. *Manganin* is an alloy of copper, manganese and nickel used for resistance coils. Pure manganese becomes appreciably magnetic only on heating; at room temperature it is paramagnetic. Some alloys (*Heusler's alloys*) of copper, aluminium and manganese are magnetic.

Manganese forms five series of compounds (apart from $\text{Na}_5\text{Mn}(\text{CN})_6$ containing 1-valent Mn and Na_3MnO_4 containing 5-valent Mn) :

- (i) **manganous salts** containing 2-valent Mn.
- (ii) **manganic salts** containing 3-valent Mn.
- (iii) **manganese dioxide** MnO_2 and salts related to it, e.g. $\text{Mn}(\text{SO}_4)_2$, containing 4-valent Mn.
- (iv) **manganates** containing 6-valent Mn.
- (v) **permanganates** containing 7-valent Mn.

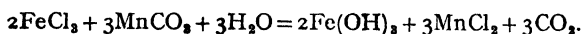
MANGANOUS SALTS

Manganous salts may be obtained by dissolving the metal or manganous carbonate in acids, but are usually prepared from manganese dioxide.

Manganous chloride is contained in the residues after the preparation of chlorine :



Since pyrolusite always contains iron the solution is yellow and contains ferric chloride FeCl_3 ; this prevents the crystallisation of the manganous chloride. In order to separate the iron, one-tenth of the filtered solution is evaporated to drive off excess of acid and is precipitated with sodium carbonate. Ferric hydroxide and manganous carbonate are thrown down. The precipitate is washed and added to the remainder of the solution. On boiling, the whole of the iron is precipitated as ferric hydroxide, manganese going into solution as chloride, and the filtered solution on evaporation deposits pink crystals of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$:



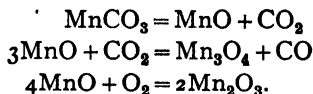
On heating the pink hydrated crystals at 200° , rose-red anhydrous MnCl_2 is formed, which gives a green solution in alcohol. The **fluoride** MnF_2 , **bromide** $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ and **iodide** $\text{MnI}_2 \cdot 4\text{H}_2\text{O}$ are known.

By heating the carbonate or any higher oxide of manganese in hydrogen, **manganous oxide** MnO is obtained as a greyish-green powder. If the hydrogen contains a trace of HCl , emerald-green crystals of the oxide are formed. Manganous oxide is also formed on heating the oxalate : $\text{MnC}_2\text{O}_4 = \text{MnO} + \text{CO} + \text{CO}_2$. Alkali hydroxide added to a solution of a manganese salt gives a white precipitate of **manganous hydroxide** $\text{Mn}(\text{OH})_2$, which in presence of air or oxygen rapidly oxidises to brown **manganic hydroxide** $\text{Mn}(\text{OH})_3$ or $\text{MnO}(\text{OH})$.

Ammonia precipitates $\text{Mn}(\text{OH})_2$ only slowly from a solution containing ammonium chloride. Probably the reaction is similar to that with magnesium salts (p. 334). The solution rapidly deposits $\text{MnO}(\text{OH})$ on exposure to air.

Manganous carbonate MnCO_3 is formed as a white precipitate on adding sodium bicarbonate to a solution of a manganous salt through which carbon dioxide is passed. (The precipitate contains manganous hydroxide if sodium carbonate is used.) It is sparingly soluble in water containing carbon dioxide to form a bicarbonate, and when moist readily oxidises in air to brown manganic hydroxide $\text{MnO}(\text{OH})$ (cf. FeCO_3). It occurs as the bright red mineral *manganese spar* (*rhodochrosite*) isomorphous with calcite ; the mineral *manganocalcite* ($\text{Mn}, \text{Ca}, \text{Mg}$) CO_3 is isomorphous with

aragonite. Manganese carbonate is decomposed by heat; at high temperatures or in presence of air a higher oxide of manganese is formed :

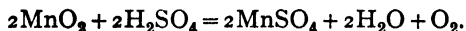


Manganous nitrate forms deliquescent crystals $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. On heating gently it decomposes and deposits manganese dioxide (p. 587).

Manganous ammonium phosphate $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ is formed as a reddish-white glittering crystalline precipitate by adding ammonium chloride, ammonia and sodium phosphate to a solution of a manganous salt. On ignition it forms the **pyrophosphate** $\text{Mn}_2\text{P}_2\text{O}_7$. This is used in the gravimetric determination of manganese.

Manganous sulphide MnS occurs as the mineral *alabandite*. It is formed as a grey mass by heating the carbonate with sulphur, or the oxide, carbonate or sulphate in hydrogen sulphide; or as a light flesh-coloured amorphous powder by precipitating a manganous salt with ammonia and ammonium sulphide. In contact with excess of ammonium sulphide it passes into a green form. Manganous sulphide dissolves readily in dilute acids, even acetic; in this way manganese may be separated from zinc, the sulphide of which is insoluble in acetic acid.

Manganous sulphate is obtained from pyrolusite by heating with concentrated sulphuric acid :



The residue is heated to dull redness to decompose ferric sulphate : $\text{Fe}_2(\text{SO}_4)_3 = \text{Fe}_2\text{O}_3 + 3\text{SO}_3$, dissolved in water and the filtered solution evaporated, when pink crystals of the hydrated salt $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ separate. The last traces of iron may be removed by boiling with a little manganous carbonate.

The salt forms a number of hydrates, *e.g.* $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ isomorphous with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ isomorphous with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. With aluminium sulphate it forms a pseudo-alum $\text{MnSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 22\text{H}_2\text{O}$. Similar double salts (which are *not* isomorphous with true alums, p. 381) are formed with ferrous iron, copper, zinc and magnesium in place of manganese.

MANGANIC SALTS

Manganic fluoride MnF_3 is obtained as a purple solid by the action of fluorine on manganous iodide, and the hydrate $\text{MnF}_3 \cdot 3\text{H}_2\text{O}$ by dissolving Mn_2O_3 in hydrofluoric acid. Anhydrous MnF_3 decomposes on heating into manganous fluoride and fluorine : $2\text{MnF}_3 = 2\text{MnF}_2 + \text{F}_2$.

Manganic chloride or **manganese trichloride** MnCl_3 is probably contained in the dark-brown solution of manganese dioxide in cold concentrated hydrochloric acid: $2\text{MnO}_2 + 8\text{HCl} = 2\text{MnCl}_3 + 4\text{H}_2\text{O} + \text{Cl}_2$. On warming, chlorine is evolved: $2\text{MnCl}_3 = 2\text{MnCl}_2 + \text{Cl}_2$.

Pure MnCl_3 is obtained by the action of dry hydrogen chloride on manganic acetate (see below); it is stable below -35° . Complex salts such as K_2MnCl_5 are known.

Manganic oxide Mn_2O_3 occurs as *braunite* and the hydrated form MnO(OH) as *manganite*. The oxide is formed as a black powder on heating any other oxide in air, e.g. $4\text{MnO} + \text{O}_2 = 2\text{Mn}_2\text{O}_3$. The hydrate MnO(OH) is formed as a dark-brown powder by passing chlorine into a suspension of manganous carbonate in water:



Excess of manganous carbonate is removed by very dilute nitric acid. When heated with nitric acid the hydrated oxide is decomposed into manganous nitrate and manganese dioxide:



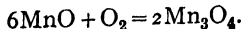
Manganic acetate $\text{Mn(C}_2\text{H}_3\text{O}_2)_3$ is obtained as a black solid by heating the crystalline nitrate $\text{Mn(NO}_3)_2 \cdot 2\text{H}_2\text{O}$ with acetic anhydride.

Manganic sulphate $\text{Mn}_2(\text{SO}_4)_3$ is a dark-green powder obtained by gently heating precipitated manganese dioxide with concentrated sulphuric acid, draining on a porous plate, washing with concentrated nitric acid and heating at 150° to expel the nitric acid:

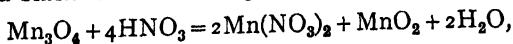


It forms alums, the caesium alum $\text{Cs}_2\text{SO}_4 \cdot \text{Mn}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ being most stable; they tend to hydrolyse in solution. Manganic sulphate forms a violet solution which deposits MnO(OH) on dilution.

Mangano-manganic oxide Mn_3O_4 (*red oxide of manganese*) occurs as *hausmannite*. It is formed as a brownish-red powder on heating manganese dioxide out of contact with air: $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$, or when any other oxide of manganese is *strongly* heated in air:



When boiled with dilute nitric acid it forms a solution of manganous nitrate and a black residue of manganese dioxide:



so that it behaves as $2\text{MnO}, \text{MnO}_2$.

Manganese dioxide occurs native as *pyrolusite*. It is prepared in the pure state by heating about 600 gm. of manganous nitrate until red fumes appear, decanting the clear liquid from the residue of lower oxides and

heating it for forty to sixty hours at 150° to 160° , when a hard lustrous black mass is formed: $\text{Mn}(\text{NO}_3)_2 = \text{MnO}_2 + 2\text{NO}_2$. If solutions of manganous salts are treated with oxidising agents such as potassium permanganate, sodium hypochlorite, ammonia and bromine, or ozone, brown precipitates are obtained which contain less oxygen than corresponds with the formula MnO_2 . Manganese dioxide is not a true peroxide but is $\text{O}=\text{Mn}=\text{O}$; it is a feebly acidic oxide and with strong bases forms manganites, e.g. CaO, MnO_2 and $\text{CaO}, 2\text{MnO}_2$, and perhaps $2\text{MnO}, \text{MnO}_2$ and MnO, MnO_2 .

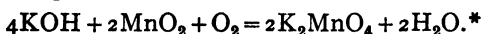
Besides its use in decolorising glass, manganese dioxide is applied (mixed with ferric oxide) as a dark-brown glaze to pottery, and is used as a depolariser in the Leclanché cell.

Manganese tetrachloride MnCl_4 is not known but a complex salt K_2MnCl_6 is said to be formed by the action of very concentrated hydrochloric acid on potassium permanganate.

Manganese disulphate $\text{Mn}(\text{SO}_4)_2$ is a powerful oxidising agent obtained by the electrolytic oxidation of manganous sulphate in fairly concentrated sulphuric acid.

MANGANATES AND PERMANGANATES

If manganese dioxide is fused with potassium or sodium hydroxide with free access to air, a green mass is formed which contains a manganate, e.g. K_2MnO_4 . The reaction is more complete with potassium hydroxide and more rapid if potassium or sodium nitrate or chlorate is added:



The dark-green mass may be dissolved in a *small* quantity of cold water forming a dark-green solution, from which on evaporation in a vacuum dark-green crystals of the manganates K_2MnO_4 or $\text{Na}_2\text{MnO}_4, 10\text{H}_2\text{O}$ are deposited. These are isomorphous with the corresponding sulphates, K_2SO_4 and $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$. Sodium manganate is used as a disinfectant, since it is a powerful oxidising agent.

Potassium manganate may also be prepared by boiling potassium permanganate with concentrated potassium hydroxide solution, when it crystallises on cooling and is filtered with asbestos:



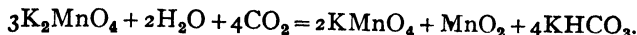
If the dark-green solution of the manganate in a little water is poured into a large volume of water a purple solution of a permanganate and a brown precipitate of hydrated manganese dioxide are formed:



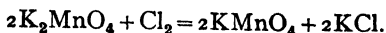
In presence of excess of alkali the reaction does not take place and the

* It should be noted that permanganate is *not* formed at this stage.

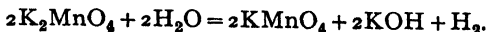
manganate is stable. The reaction occurs completely if the alkali produced is removed by adding an acid, even carbonic acid :



Potassium permanganate may be obtained from the manganate by passing chlorine into the solution :



It is also prepared by the electrolytic anodic oxidation of the manganate solution :



In the laboratory preparation of potassium permanganate a powdered mixture of 50 gm. of potassium hydroxide and 25 gm. of potassium chlorate is fused on one iron sand-bath covered with a second one. To the fused mass 50 gm. of finely powdered pyrolusite are added gradually, stirring with an iron rod. The heating is continued until the mass stiffens : it is cooled and extracted with 1 litre of water. The liquid is boiled and carbon dioxide passed in until a drop of the liquid placed on filter paper gives a purple colour (no green). The liquid is allowed to settle, filtered through asbestos, evaporated to 300 c.c. and filtered hot through asbestos. On cooling potassium permanganate crystallises. A further crop is obtained by evaporating the mother liquor to 100 c.c.

Potassium permanganate forms deep purple-red brilliant rhombic prisms which have a green iridescence. It is rather sparingly soluble in water to a deep-purple solution which is opaque unless it is quite dilute. The crystals evolve oxygen on heating and fall to a black powder :

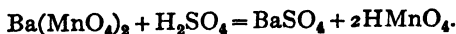


At a red heat the manganate is decomposed into manganite and oxygen :

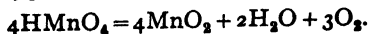


Potassium permanganate forms with sulphur and charcoal mixtures which deflagrate when kindled.

Manganic acid is not known in the free state since manganates when treated with other acids do not give manganic acid but permanganates. Permanganic acid HMnO_4 is formed in solution by boiling a solution of manganous sulphate or nitrate with lead dioxide and nitric acid, or with sodium bismuthate and nitric acid in the cold. A pure solution is prepared by adding dilute sulphuric acid to a solution of barium permanganate :



Permanganic acid forms a deep-purple solution. The acid is a powerful oxidising agent ; it is unstable and the solution decomposes with evolution of oxygen and deposition of manganese dioxide :



When powdered potassium permanganate is added in small quantities at a time to cooled concentrated sulphuric acid, a dark-green solution is formed which is liable to explode violently in contact with traces of organic matter or even spontaneously and should never be prepared in quantity. When treated with ice-cold water dark-brown drops of **manganese heptoxide** Mn_2O_7 separate :

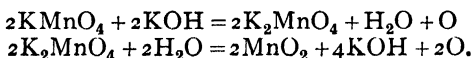


Manganese heptoxide forms a violet vapour on warming, but explodes violently at 55° or in presence of organic matter. With water it forms a violet solution of permanganic acid, of which it is the anhydride.

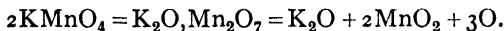
The old formula of potassium permanganate is $\text{K}_2\text{Mn}_2\text{O}_8$ (*i.e.* $\text{K}_2\text{O}, \text{Mn}_2\text{O}_7$) but the freezing point and conductivity of the solution show that the salt is KMnO_4 .

Reactions of potassium permanganate.—Potassium permanganate is a powerful oxidising agent. The action is different in alkaline, neutral and acid solutions.

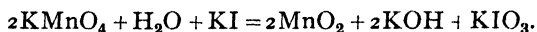
(1) In *alkaline solutions* the permanganate is first reduced to green manganate. The solution then deposits brown manganese dioxide and becomes colourless :



Hence two molecules of permanganate in *alkaline* solution give *three* atoms of available oxygen when reduced to manganese dioxide :

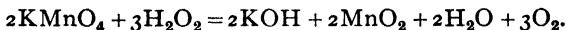


Alkaline permanganate oxidises iodides to iodates :

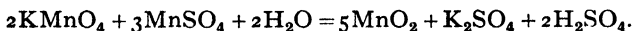


(2) In *neutral solutions* the permanganate is generally reduced to manganese dioxide, which precipitates (see above).

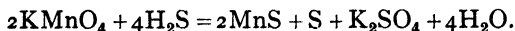
Hydrogen peroxide with neutral permanganate gives a precipitate of manganese dioxide and oxygen is evolved :



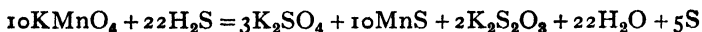
A manganous salt is oxidised in neutral solution in presence of zinc sulphate or zinc oxide to manganese dioxide (which may form $\text{ZnO}, 2\text{MnO}_2$) :



Hydrogen sulphide reacts with neutral 1 per cent. permanganate :

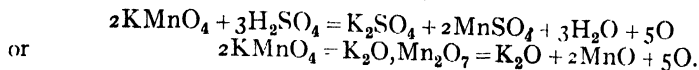


The reaction is really more complicated :

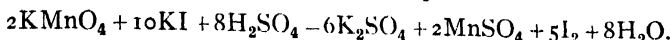


At the beginning of the reaction some dithionate ($\text{K}_2\text{S}_2\text{O}_8$) is formed.

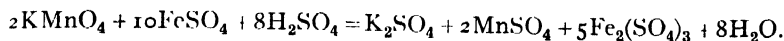
(3) In *acid solutions* two molecules of permanganate are reduced to a manganous salt and *five* atoms of oxygen become available :



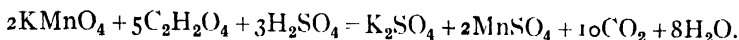
In acid solutions iodine is liberated from potassium iodide :



Ferrous salts are oxidised to ferric salts :

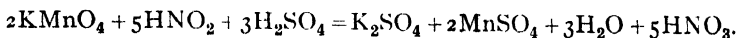


Oxalic acid is oxidised to carbon dioxide :

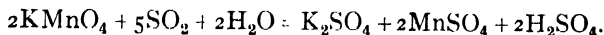


This reaction is slow at first, unless some manganous sulphate is added, which acts as a catalyst.

Nitrites are oxidised to nitrates :

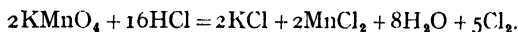


Sulphur dioxide is oxidised to sulphuric acid :



The reaction with hydrogen peroxide has been described (p. 109). The reactions are accelerated by the presence of manganous salts, which act catalytically.

In presence of free hydrochloric acid, chlorine may be evolved from permanganate solution :



This may be prevented to some extent by adding a few grams of manganous sulphate and titrating in the cold. The manganous salt greatly increases the velocity of the primary reaction (*e.g.* oxidation of ferrous salt), but not that of the oxidation of hydrochloric acid.

Cyanogen compounds.—Potassium cyanide gives with solutions of manganous salts a yellowish-grey precipitate, sometimes said to be **manganous cyanide** $\text{Mn}(\text{CN})_2$, soluble in excess of the reagent to a yellow solution of **potassium manganocyanide** analogous to the ferrocyanide, which crystallises as a deep-blue solid $\text{K}_4\text{Mn}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. By evaporating this solution in air the manganese is oxidised and the solution contains **potassium manganicyanide** $\text{K}_3\text{Mn}(\text{CN})_6$ analogous to the ferricyanide. This forms large red prisms. The resemblance between manganese and iron is apparent and the corresponding salts are isomorphous.

The **atomic weight of manganese** was determined from the ratios $\text{MnCl}_2 : 2\text{AgCl}$ and $\text{MnBr}_2 : 2\text{AgBr}$. The valency follows from the atomic heat and from the isomorphism of manganous and ferrous compounds.

CHAPTER XXXIII

IRON

THE eighth group of the Periodic System comprises what Mendeléeff called the **transitional elements** (p. 254); their atomic numbers are:

Iron - - 26	Ruthenium - 44	Osmium - - 76
Cobalt - - 27	Rhodium - 45	Iridium - - 77
Nickel - - 28	Palladium - 46	Platinum - - 78

The **inert gases** are now often put in a sub-group of Group VIII:

Helium - - 2	Argon - - 18	Xenon - - 54
Neon - - 10	Krypton - 36	Emanation - 86

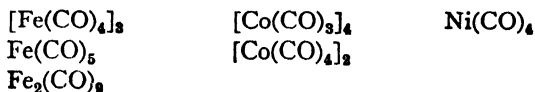
The atomic weights in each of the three periods of Mendeléeff's transitional elements differ little from one another, a behaviour similar to that shown by the rare-earth elements (p. 254).

The physical and chemical properties of the elements are also closely related; the platinum metals are very similar and are difficult to separate, as are also cobalt and nickel. The elements in the vertical columns (p. 252) show close resemblances; ruthenium and osmium form higher oxides MO_4 . All the elements form lower basic oxides. The resemblance between the metals of the iron group and the platinum metals is somewhat remote and is chiefly confined to the ease with which all metals of Group VIII form analogous *complex compounds*: potassium ferrocyanide $\text{K}_4\text{Fe}(\text{CN})_6$, potassium cobaltinitrite $\text{K}_3\text{Co}(\text{NO}_2)_6$, potassium chloroplatinate K_2PtCl_6 . Nickel shows this property to a much smaller degree.

Iron, cobalt and nickel are magnetic metals with high melting points, oxidise in the air at a red heat, and decompose steam at high temperatures. The oxides MO are all known and are strong bases. The sesquioxides M_2O_3 are also basic, but their salts are stable only in the case of iron. Oxides of the type M_3O_4 are also known; their salts, if they exist, are very unstable so that these oxides probably have the formula $\text{MO}, \text{M}_2\text{O}_3$, or $\text{M}(\text{MO}_2)_2$, in which M_2O_3 functions as a feebly acidic oxide and MO as a base. Ferric oxide forms ferrites, *e.g.* NaFeO_2 or $\text{Na}_2\text{O}, \text{Fe}_2\text{O}_3$. Iron forms compounds of an unknown acidic trioxide FeO_3 , *e.g.* potassium

ferrate K_2FeO_4 , in which 6-valent iron shows a resemblance to manganese and chromium in K_2MnO_4 and K_2CrO_4 . The metals iron, manganese and chromium have similar physical properties.

Iron, cobalt, and nickel combine with carbon monoxide to form **carbonyls** :



IRON

History.—Metallic iron was known in pre-Dynastic Egypt (before 3400 B.C.) but was exceedingly scarce and used only as beads for jewellery (Flinders Petrie). It may have been obtained from meteoric iron since it contains nickel. Iron of this early period is also known for Mesopotamia, some possibly terrestrial. The metal came into general use in Egypt only much later (about 1500 B.C.) The use of iron seems to have spread from the Hittites in Asia Minor. It was much used by the Assyrians about 600 B.C. In the Mycenaean (pre-Classical Greek) period described by Homer iron was still a rare metal—a lump of iron is the prize given to Achilles (*Iliad*, xxiii, 834)—but the Greeks brought with them the use of iron. The Etruscans worked the mines of Elba, later taken over by the Romans who also worked the mines of Spain and Noricum. Iron seems to have been worked at an early date in India.

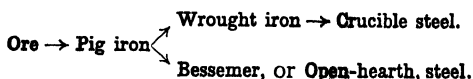
Occurrence.—Iron does not occur to any great extent in the free state on the earth although meteorites, which sometimes consist of metallic iron with from 3 to 30 per cent. of nickel and some occluded hydrogen, show that it must be present in the solar system. Since meteoric iron contains nickel it does not easily rust. Iron compounds occur in the soil, in green plants and in haemoglobin, the red colouring matter of blood.

The **ores** of iron are plentiful but relatively few in number, although the element occurs in nearly every mineral. The black ferrosferric oxide Fe_3O_4 occurs as the important ore *magnetite*, so called because certain varieties (lodestone) are permanently magnetic. This is not found to any extent in the British Isles but occurs in Siberia, Norway, Lapland, Sweden, Germany and North America. It contains when pure over 70 per cent. of iron and is the richest ore. Ferric oxide Fe_2O_3 occurs as *haematite*, sometimes crystalline and red, or if black giving a red streak when drawn over an unglazed porcelain plate. It also occurs in earthy granular and nodular forms and is found in Belgium, Russia, Sweden, the island of Elba, south of Lake Superior and in England in the Furness district in Lancashire. Hydrated ferric oxide is *limonite*, occurring in kidney-shaped amorphous masses in South Wales, the Forest of Dean, France, Germany and at Bilbao in Spain. The so-called *bog iron ores* are hydrated ferric oxide and occur in large quantities in Ireland, Sweden and North Germany.

The only remaining important ore is ferrous carbonate FeCO_3 occurring either alone as *siderite*, *chalybite* or *spathic iron ore* in the Alps and in Hungary, or mixed with clay as *clay-ironstone*, or with clay and coal as *blackband-ironstone*. The hydrated oxide and the impure forms of the carbonate are the most important British ores. Pyrites cinders, chiefly ferric oxide, from the manufacture of sulphuric acid may be desulphurised by roasting and smelted for iron. The value of an ore of iron depends on its freedom from impurities (S, P, As, etc.) which are detrimental to the resulting metal.

The metallurgy of iron.*—Three varieties of commercial iron are made:

(1) cast iron or pig iron; (2) malleable iron or wrought iron; (3) steel. The order in which they are prepared from the ore is roughly as follows:



The extraction of iron from the ores involves a number of processes.

(1) **Preliminary roasting** or calcination is used with carbonate or hydrated ferric oxide ores to drive off carbon dioxide and moisture and leave ferric oxide Fe_2O_3 . It is carried out by stacking the ore with a little coal in heaps or shallow kilns or shaft-furnaces, and regulating the temperature and supply of air so that most of the moisture, carbon dioxide, sulphur and arsenic are expelled; ferrous oxide (FeO) is also converted into ferric oxide (Fe_2O_3) to avoid the production of ferrous silicate in the slag during smelting. The ore is also rendered more porous. Powdery ore is agglomerated by sintering or briquetting.

(2) **Smelting** or reducing the ore with carbon in the blast-furnace.

The blast-furnace (introduced in a simple form about 1500) consists (Fig. 238) of an outer shell of steel plates, lined with refractory bricks. It is 50 to 100 ft. high, the greatest width being up to 24 ft. at the "boshes". The mouth is closed with a *cup-and-cone* through which the charge of ore, limestone and fuel is fed intermittently by lowering the cone. (In large modern furnaces a double cup-and-cone is used, which prevents the escape of gas on opening the lower cone.) The gas passes away through a pipe to a *dust-catcher* and *washer* and is utilised by burning in the Cowper stoves (see below) for heating the air-blast. The furnace below the boshes narrows gradually to a *hearth* at the base, pierced with holes for a number of water-jacketed iron blowing-pipes or *tuyeres*, through which air is forced from an annular pipe by powerful blowing-engines. The hearth is also pierced with a hole stopped with clay from which the molten iron is periodically tapped into sand moulds on the ground, and a *slag-notch* at a higher level through which the molten slag runs continuously from above the fused metal. About 3 to 5 tons of air are passed through the furnace

* Turner, *The Metallurgy of Iron*, 5th edit., 1918; Stoughton, *The Metallurgy of Iron and Steel*, 4th edit., New York, 1934; Harbord and Hall, *The Metallurgy of Steel*, 7th edit., 2 vols., London, 1923.

per ton of iron made, the power for working the blowing-engines being supplied by coke-oven gas obtained in producing the coke for the blast-furnace. Coal is still used in Scotch furnaces but elsewhere hard oven-coke or sometimes charcoal is employed.

The composition of the charge for the blast-furnace is 1 ton of coke, 8 to 12 cwt. of limestone to form the slag (consisting of calcium and aluminium silicates) and so much ore (say $2\frac{1}{2}$ tons) as produces 1 ton of iron. The process is continuous and goes on day and night without interruption.

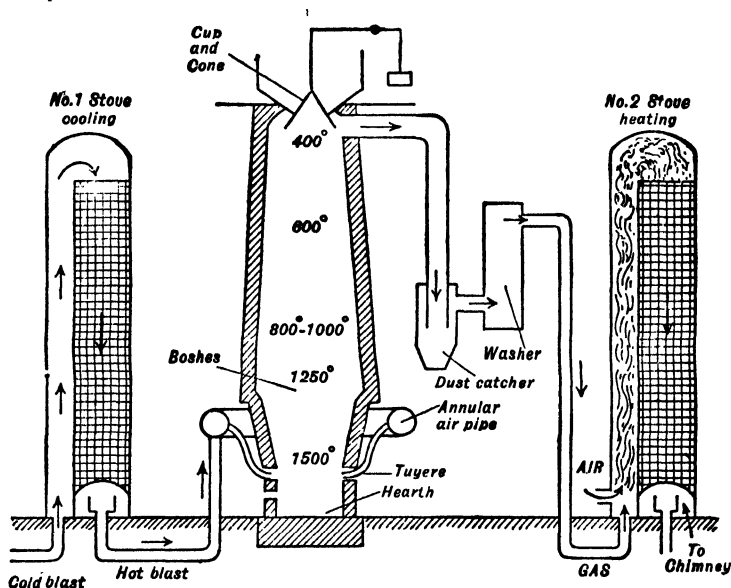


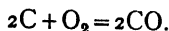
FIG. 238.—Blast-furnace and Cowper stoves.

The air for the blast is pre-heated to 700° to 800° by passing through Cowper stoves consisting of tall iron cylinders lined with firebricks, packed with chequer brickwork with a circular gas flue on one side. Part of the gas from the blast-furnace together with sufficient air to burn it passes through until the bricks are red hot. The products of combustion escape to a chimney (not shown). The gas is then turned through a second stove and the air blast to the tuyeres is sent through the first one until the brickwork has cooled. The two stoves are thus alternately used as absorbers and emitters of heat, or as heat-regenerators. This economises fuel and the blast-furnace works at a higher temperature.

The blast-furnace gas consists of nitrogen and carbon monoxide with some carbon dioxide. It is mostly used in heating the stoves, although in some works it is partly used to raise steam for the blowing-engines or as fuel for gas engines.

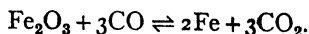
In some cases a *dry blast* is used, the air being first dried by refrigeration or by adsorbing moisture in silica gel. In this way loss of heat by the reaction: $C + H_2O \rightleftharpoons CO + H_2$, in the blast-furnace is prevented.

Chemical reactions in the blast-furnace.—The oxygen of the blast unites with carbon at a very high temperature in the hearth to produce largely carbon monoxide, which rises through the furnace:



The temperature of the charge passing down the furnace increases continually from the mouth to the hearth.

Above the boshes at a dull-red heat the ferric oxide is reduced by the carbon monoxide to spongy iron:

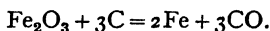


The reaction is reversible and the escaping gas contains both CO and CO₂. In this upper zone the limestone is decomposed:

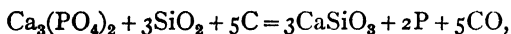


and some carbon dioxide is reduced to monoxide: $CO_2 + C \rightleftharpoons 2CO$. The spongy iron absorbs sulphur from the fuel.

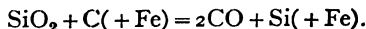
Near the centre of the furnace, at a bright-red heat, finely divided carbon is deposited by the reaction: $2CO \rightleftharpoons CO_2 + C$. This and the carbon of the charge complete the reduction:



Phosphorus is produced by reduction of phosphates in the ore:



and the phosphorus is absorbed by the iron. At a higher temperature some silicon is formed by the reduction of silica by carbon in presence of iron, and alloys with the iron:



The silica and lime now form a fusible slag which usually contains some calcium sulphide. Manganese is also formed by reduction of manganese compounds in the ore, *e.g.* $Mn_2O_3 + 3C = 2Mn + 3CO$.

At a white heat in the lowest part of the furnace the spongy iron containing carbon, silicon, manganese, sulphur and phosphorus fuses to molten cast iron which is tapped off from time to time into sand moulds to form pig iron, or is sent in the fused state to the steel furnaces.

Cast iron.—*Pig iron* contains 2.2 to 4.5 per cent. of carbon, with silicon, manganese, sulphur and phosphorus. When the cooling is rapid, the silicon content small and the manganese high, *white pig iron* is formed in which all the carbon is in the form of iron carbide Fe₃C (*cementite*); it is brittle and coarsely crystalline, and dissolves nearly completely in dilute hydrochloric acid evolving a mixture of hydrogen and hydrocarbons. If, however, the molten iron containing at least

2.5 per cent. of silicon is slowly cooled most of the carbon separates in the form of fine laminae of graphite, the iron at the same time becoming softer and of a finer texture; on solution in hydrochloric acid it evolves chiefly hydrogen and leaves a black residue of graphite. This variety of cast iron is known as *grey pig iron*. An intermediate variety is called *mottled pig iron*. The solubility of carbon in pure iron is 4.25 per cent., but much more is dissolved if manganese is present.

Malleable or wrought iron.—This is nearly pure iron containing only from 0.12 to 0.25 per cent. of carbon, and melts at a higher temperature than cast iron. Malleable iron contains less than 0.5 per cent. of total impurities (carbon, sulphur, phosphorus and silicon).

Malleable iron is obtained from cast iron by the **puddling process**, invented by Henry Cort of Lancaster in 1784. The cast iron is fused in a reverberatory furnace (p. 306) the hearth of which is lined with haematite which oxidises the carbon: $3C + Fe_2O_3 = 2Fe + 3CO$, the carbon monoxide bubbling through the molten iron. Sulphur, phosphorus and silicon are oxidised and pass into the slag. When the metal becomes pasty it is formed into lumps or “blooms” which are beaten under steam hammers to squeeze out the slag. The iron although not fused *welds* together to a coherent mass at a bright-red heat.

Malleable iron is tough and fibrous; its property of welding, whereby two pieces when heated to redness unite on hammering, is exceedingly valuable and is applied in various ways by the blacksmith. Its softness is not appreciably altered by heating to redness and quenching in water, whereas steel then becomes very hard. Wrought iron has now largely been replaced by mild steel.

Wrought iron containing combined phosphorus is brittle at the ordinary temperature and is said to be *cold-short*; combined sulphur, probably FeS, renders the metal brittle at a red heat, when it is known as *red-short*.

If cast iron is cast in a metal mould so as to cause rapid cooling the cementite may be decomposed by heating the casting, embedded in haematite, for several days. The combined carbon in the surface is oxidised and that from the interior diffuses out to replace it. Finally the carbon content is reduced to that of steel, and a *malleable casting* is produced. Sometimes the cementite in the interior is caused to decompose with separation of fine graphite and the iron becomes soft. The result is a “black-heart casting”, white outside with a black core.

Steel.—This is iron which has been fused in the process of manufacture and contains from 0.15 (very soft steel) to 1.5 per cent. or more (very hard steel) of carbon, part at least combined in the form of iron carbide or cementite Fe_3C . It also contains small amounts of other elements but the impurities of the cast iron, viz. silicon, phosphorus, sulphur and manganese, have been largely removed.

Analyses of cast iron and the steel made from it illustrate this :

	Fe	C	Si	P	Mn	S
Cast iron	- 93.2	1.0	1.4	2.5	1.8	0.1
Steel	- 99.3	0.18	0.004	0.02	0.44	0.042

Steel also differs from iron in acquiring a "temper" by heating and quenching ; it becomes soft when heated and slowly cooled.

Steel may be made (1) from pure wrought iron by increasing the amount of combined carbon, (2) from cast iron by removing part of the carbon and taking out the impurities. In modern processes the second method is used and the main processes are :

- (1) The Bessemer process (Henry Bessemer, 1855).
- (2) The Siemens-Martin or open-hearth process (1864).

When wrought iron is made from pure oxide ores by reduction with charcoal it is converted into steel by the *cementation process*. Bars of wrought iron are heated surrounded with charcoal for one or two weeks. Absorption of carbon occurs, the carbonisation spreading slowly through the mass and converting the iron into steel. The surface of the bars is covered with blisters, and the blister steel is fused in plumbago crucibles to form *cast steel* or *crucible steel*. This process has now been superseded by the electric furnace for high-quality steels for tools, etc.

The Bessemer process.—In this, molten pig iron from the blast-furnace is run into a *converter* (Fig. 239), a large pear-shaped iron vessel lined with refractory silica bricks. The converter holds 10 tons of metal and is supported on trunnions, cold air being forced by a pipe to a hollow perforated bottom from which it bubbles through the molten metal. The charging is carried out through the open mouth with the converter horizontal, and blowing is begun. The converter is then swung into a vertical position and blowing continued.

Silicon and manganese are first oxidised (producing most of the heat) and pass into the slag ; then a portion of the iron is oxidised. The resulting ferric oxide removes the carbon, forming carbon monoxide which is now freely evolved and burns at the mouth of the converter as an orange-yellow flame edged with blue and shot through by showers of sparks. After six to eight minutes the flame sinks, indicating that the carbon has been removed. The converter is again tilted, the blast is stopped, and the requisite amount of *spiegel* added. *Spiegeleisen* is iron containing manganese and carbon. The converter is blown again for a short time to mix the charge, when the manganese reduces any ferrous oxide and the carbon

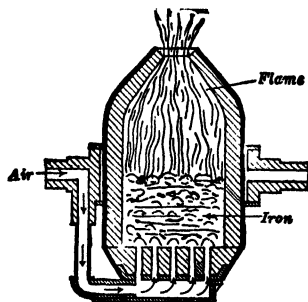


FIG. 239.—Bessemer converter.

unites with the iron to form steel. This process of carburising the iron was introduced by Mushet in 1856.

By further tilting the converter, the molten steel is poured into ladles supported by travelling cranes, from which it is run into moulds. A little aluminium, silicon-iron alloy (*silicon-spiegel*) or titanium-iron alloy may be added to prevent blow-holes in the castings due to bubbles of gas (nitrogen, carbon monoxide) which will combine or react with the aluminium, silicon or titanium. According to the percentage of carbon added, various kinds of steel are produced: *tool steel* (0.9 to 1.5 per cent. C), *structural steel* (0.2 to 0.6 per cent. C) and *mild steel* (0.2 per cent. or less C).

Ores of iron containing phosphates give cold-short iron. Such "phosphatic ores" may be worked by the **Thomas and Gilchrist process** (1879), in which the silica ("acidic") lining of the converter is replaced by a "basic" lining of magnesia and lime prepared by calcining dolomite. Limestone is first charged into the converter along with coke and the blast is turned on. Molten pig iron is then run in and the blast continued. Silicon and manganese are first burnt out and then the phosphorus (producing most of the heat) and carbon are oxidised simultaneously. When the carbon is burnt out the flame drops and the blast is prolonged to burn out the remaining phosphorus. The phosphorus pentoxide combines with the lime from the limestone added (*not* the converter lining) to form a slag. *Spiegeleisen* is added in the ladle (*not* in the converter). The slag ("basic slag") contains calcium phosphate and is used as a fertiliser.

The steel pigs produced by casting are annealed in underground furnaces ("soaking-pits") heated by blast-furnace gas, and are then passed through the rolling mills for the production of steel bars.

The open-hearth process.—This was suggested by Reaumur in France in 1722 and by John Payne in 1728 but was first successfully worked in 1864 by the brothers Martin in France, who used the regenerative heating

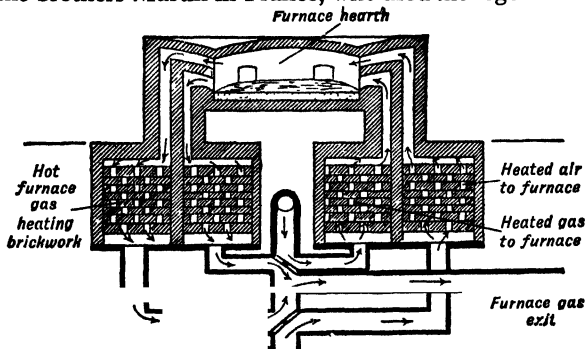


FIG. 240.—Open-hearth steel furnace.

process of Sir William Siemens. It is carried out on a large flat hearth enclosed in a furnace (Fig. 240) heated by producer gas. The air and gas are supplied through separate regenerators of chequer brickwork used in pairs and alternately traversed by the hot products of

combustion, and the gas and air, as in the Cowper stoves. The hearth is lined with silica in the "acid" process or with calcined magnesite or dolomite in the "basic" process. The charge consists of pig iron (part of which may be run in liquid from the blast-furnace), steel scrap and haematite, with limestone in the basic process. By the action of the haematite part of the carbon is burnt out of the cast iron and fluid steel remains. The subsequent operations are the same as in the Bessemer process. The furnace may be made to tilt and discharge a portion of its contents into a ladle. The operation lasts 8 to 10 hours; it is more easily controlled than the Bessemer process and is very largely used in Great Britain although the Bessemer process holds its own in America.

A very pure (*Armco*) iron containing less than 0.1 per cent. of total impurity is made by a modification of the open-hearth process. It is almost rustless.

Electric furnaces are used in the production of special high-quality steels. They are mostly on the arc principle and consist of refractory crucibles containing two (or more) large vertical carbon electrodes between which an electric arc is struck. Such furnaces are more especially used for the production of *alloy steels*, containing nickel, chromium, vanadium and molybdenum.

The properties of steel.—The properties of steel depend largely on the content of carbon and the heat-treatment: low-carbon steels are soft like wrought iron and are known as *mild steel*; with more carbon the ductility falls, whilst the tensile strength increases up to the limiting percentage of 1.5 of carbon. Wrought iron and steel are malleable and may be welded. The melting point of steel is lower than that of wrought iron.

The properties of steel depend on the *heat-treatment* to which the metal has been subjected. If steel is heated to redness and quenched in cold water it becomes as hard and brittle as glass. If it is now heated to various temperatures the resulting metal possesses properties depending on the temperature. This operation is known as *tempering*, and the temperature is judged by the colour of the thin film of oxide produced on a bright surface of the metal:

- 230°: light straw colour: used for razor blades.
- 255°: brownish-yellow: used for penknives and axes.
- 277°: purple: used for cutlery.
- 288°: bright blue: used for watch-springs and swords.
- 290°–316°: dark blue: used for chisels and large saws.

Allotropic forms of iron.—There are three allotropic modifications of pure iron. (1) α -iron (the chief constituent of wrought iron) is stable below 900°, soft, magnetic, and capable of dissolving but little iron carbide Fe_3C . (2) γ -iron, produced by heating above 900°, is non-magnetic but differs from the other two varieties in forming solid

solutions with iron carbide. (3) δ -iron (which may be identical with α -iron) is formed at 1400° :



When steel containing carbon and also nickel or manganese is heated and quenched it forms a homogeneous non-magnetic solid solution of cementite in γ -iron, which is called *austenite* and has a structure of large crystals which are relatively soft. The nickel or manganese retards the conversion of γ -iron into α -iron, which would otherwise occur below 900° , the austenite becoming a heterogeneous mixture of α -iron + cementite. A carbon steel which is not stabilised by adding nickel or manganese forms on heating and quenching a very hard steel with a needle-like structure which is called *martensite* and is a primary stage in the breaking down of austenite to iron and cementite.

By less rapid cooling of iron containing only a little carbon a mixture of crystals of pure iron (*ferrite*) and *pearlite*, which is a finely laminated eutectoid structure of alternate layers of α -ferrite and cementite, is formed. A very finely laminated pearlite is called *sorbite*. By more rapid cooling *troostite* is formed. When iron containing more carbon is cooled slowly a mixture of cementite and pearlite is deposited. On slow cooling cementite breaks up into soft ferrite and scales of graphite.*

The change at 760° formerly called $\alpha \rightarrow \beta$, when iron loses its ferromagnetism, is not a phase- but a magnetic-transformation. The thermal change taking place is the cause of *recalcence*, the sudden re-heating of a mass of red-hot iron on cooling.

Wrought iron is *case-hardened* by heating in contact with carbon or potassium ferrocyanide, when a surface-layer of steel is produced. *Armour-plate* is made by case-hardening a sheet of soft steel on one side and then spraying it with cold water. It is pierced in a clean hole by a soft-nosed shell, whereas hard steel splits in pieces. Nickel-chrome steels form very tough armour-plates. A very hard surface of iron nitrides, e.g. Fe_3N , is formed by heating steel at 650° in an atmosphere of ammonia; "nitrided" steel has been used for lining the cylinders of motor engines.

Properties of iron.—The soft iron wire used for binding flowers contains about 99.7 per cent. of Fe. Still purer iron is obtained by the electrolysis of a solution of ferrous ammonium sulphate or of ferrous chloride. It is very brittle and may easily be powdered. The powder may be formed into a coil by adhesive and such a "Pupin coil", with very low hysteresis losses, is used in some electrical devices. By fusing the electrolytic iron in an electric vacuum furnace pure iron is obtained. It is a soft almost white metal. It is permeable to hydrogen at a red heat, and burns brilliantly in oxygen when heated to redness. *Reduced iron* is a black or grey powder obtained by heating ferric oxide in hydrogen; when

* Simons and Gregory, *The Structure of Steel*, 1942.

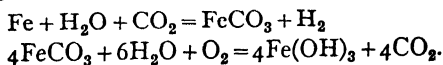
prepared from pure oxide (from the nitrate) by reduction at 450° it is pyrophoric and burns when exposed to air.

Iron readily occludes hydrogen, nitrogen and carbon monoxide, the solubility increasing with rise in temperature and showing a marked alteration about 940° .

Iron does not easily amalgamate with mercury, but an amalgam is obtained by rubbing iron powder with mercuric chloride and water, or by the action of sodium amalgam on ferrous chloride solution.

The rusting of iron.—Iron when exposed to ordinary moist air is quickly corroded to a reddish-brown rust, consisting chiefly of hydrated ferric oxide of the approximate composition $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, although this is not a definite compound. The conditions under which rusting takes place have been investigated by several experimenters, with somewhat divergent results.* The homogeneity or otherwise of the metal and its purity affect the results. The presence of water is essential and according to some experimenters the presence of carbon dioxide or acidity is also necessary. Freshly-formed rust usually contains considerable quantities of ferrous hydroxide and carbonate, indicating the formation of these compounds as an early stage in the corrosion of the metal.

Crace-Calvert (1871) and Crum Brown (1888) suggested the following reactions leading to the formation of rust :



According to G. T. Moody (1906), pure iron does not rust in the presence of water and air if every trace of carbon dioxide is excluded. The iron first passes into solution, when carbon dioxide is present, as ferrous bicarbonate $\text{Fe}(\text{HCO}_3)_2$ which then undergoes oxidation by dissolved oxygen with precipitation of ferric hydroxide. The addition of alkalis to the water, by diminishing the content of carbonic acid, retards the rusting of iron.

The following simple experiments throw some light on what happens in rusting (Fig. 241).

EXPT. I.—Take four lots, (a), (b), (c), (d), of clean iron nails.

(a) Boil ordinary tap-water in a test-tube until it begins to “bump”, showing that dissolved air has been expelled. Drop the nails (a) into the water and boil again for half a minute. Pour melted vaseline over the surface of the water. This excludes air, so that iron and water alone are present.

* J. N. Friend, *The Corrosion of Iron and Steel*, 1911; U. R. Evans, *Metallic Corrosion Passivity and Protection*, 1946; *An Introduction to Metallic Corrosion*, 1948.

(b) Place nails (b) in a test-tube full of ordinary water. In this case iron, much water, and air are present.

(c) Place nails (c) in a test-tube with a few drops of water. In this case iron, a little water, and air are present.

(d) Place nails (d) in a desiccator over sulphuric acid. In this case iron and air alone are present.

Leave the four specimens for a few days, and examine the iron. Rusting should have occurred only in cases (b) and (c).

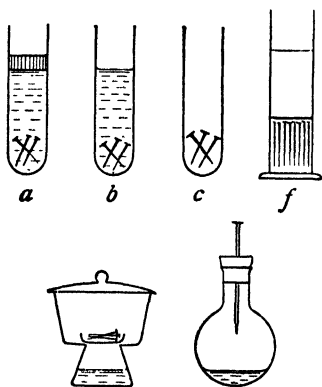


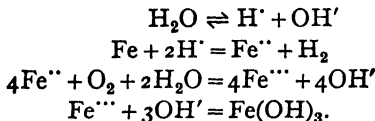
FIG. 241.—Experiments on the rusting of iron.

(e) Pour 100 c.c. of 15 per cent. caustic potash solution into a 500 c.c. flask fitted with a partly bored cork, and shake. Allow the flask to stand for two days. Boil a large bright nail with distilled water as described above (a), and push it through the cork into the flask, leaving a short length outside. Allow to stand for a few days. The part of the nail inside the flask which is exposed to air and water vapour in the absence of carbon dioxide does not rust, whilst the part outside, exposed to ordinary air, will rust.

(f) It will be noticed in Expt.

(b) that the undersides of the nails remain bright, and rust is deposited on the top exposed to air. This indicates that the iron passes into solution, and the solution is then oxidised by the air. Pack a number of bright nails tightly in a jar, cover them with a piece of filter-paper, and pour boiled distilled water into the jar. Rust is deposited *above* the filter-paper.

According to another theory of rusting, the different parts of a piece of iron act as poles of voltaic cells and solution of the metal occurs as the result of local action. Lambert (1912), who took great care to exclude carbon dioxide, found that homogeneous iron does not rust even in ordinary air, but ordinary iron rusts in the absence of carbon dioxide:



EXPT. 2.—Prepare a 1½ per cent. solution of agar-agar in hot water, and add a little potassium ferricyanide and phenolphthalein. Pour some of the solution over some clean iron nails in a glass dish. The agar sets to a jelly. After some hours the anodes become blue from reaction of ferri-

cyanide with ferrous ions, and the cathodes red from the caustic alkali formed. The cause of rusting on this theory is electrolytic.

Iron is protected from rusting by painting, or whitewashing with lime. Pipes are also protected by heating and dipping them into a solution of coal-tar pitch in coal-tar naphtha, when an impervious coating is formed (*Angus Smith's compound*). In the *Barff process*, the iron is heated to redness and steam blown over it, when an adherent layer of ferrosferric oxide is formed. This is used in treating cans for fruit, etc., instead of tinning. The layer of oxide is removed by heating with water containing magnesium chloride, which explains the corrosive action of sea-water on boilers.

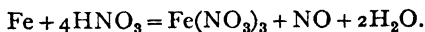
Passive iron.—Iron is rendered passive by immersion in fuming nitric acid, chloric acid, chromic acid, or hydrogen peroxide, or by making it the anode in electrolysis. The metal is then insoluble in dilute acids and does not precipitate copper from a solution of copper sulphate (Keir, 1790). The passivity is removed by touching with ordinary iron under the surface of dilute sulphuric acid. The passivity is due to a film of ferric oxide; it is removed by heating in hydrogen and it is possible to dissolve out the iron leaving the transparent skin of oxide by anodic electrolysis in salt solution.

IRON COMPOUNDS

Iron readily dissolves in dilute hydrochloric or sulphuric acid, producing **ferrous salts** containing the bivalent **ferrous ion** : $\text{Fe} + 2\text{H}^+ = \text{Fe}^{++} + \text{H}_2$. In cold dilute nitric acid no gas is evolved but the acid is reduced and ferrous and ammonium nitrates are formed :



In warm dilute nitric acid iron dissolves to form ferric nitrate with evolution of nitric oxide :

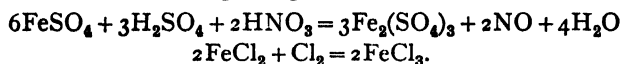


Solutions containing the ferrous ion are nearly colourless, but usually possess a green tinge due apparently to the presence of traces of the ferric ion Fe^{+++} .

The ferrous ion is readily oxidised to the trivalent **ferric ion** Fe^{+++} , which is almost colourless, the yellow, red or brown colour of ordinary solutions of ferric salts being due to the undissociated compound, to basic compounds, or to colloidal ferric hydroxide formed by hydrolysis. If these brown solutions are mixed with concentrated nitric acid they become nearly colourless ; with concentrated hydrochloric acid they become deep yellow, the colour of undissociated ferric chloride.

Ferrous salts are oxidised to ferric salts (i) by atmospheric oxygen in neutral solutions, when insoluble basic ferric salts are precipitated ;

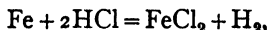
(ii) by chlorine or bromine : $2\text{Fe}^{++} + \text{Cl}_2 = 2\text{Fe}^{+++} + 2\text{Cl}'$; the reaction with iodine is reversible : $2\text{Fe}^{++} + \text{I}_2 \rightleftharpoons 2\text{Fe}^{+++} + 2\text{I}'$, so that ferric chloride liberates iodine from potassium iodide and iodine oxidises ferrous chloride to ferric chloride ; (iii) by silver nitrate : $\text{Fe}^{++} + \text{Ag}' = \text{Fe}^{+++} + \text{Ag}$; (iv) by boiling with nitric acid or *aqua regia* :



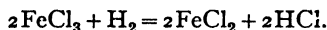
Ferric salts are reduced to ferrous salts (i) by nascent hydrogen in acid solution, say by zinc and hydrochloric acid : $\text{Fe}^{+++} + \text{H} = \text{Fe}^{++} + \text{H}'$; (ii) by hydrogen sulphide : $2\text{FeCl}_3 + \text{H}_2\text{S} = 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$; (iii) by sulphur dioxide : $2\text{FeCl}_3 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{FeCl}_2 + \text{H}_2\text{SO}_4 + 2\text{HCl}$; (iv) by stannous chloride : $2\text{FeCl}_3 + \text{SnCl}_2 = 2\text{FeCl}_2 + \text{SnCl}_4.$

FERROUS SALTS

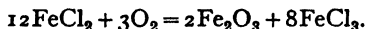
Anhydrous ferrous chloride is obtained in white (usually grey) lustrous scales on heating iron in a stream of hydrogen chloride :



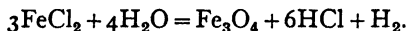
or by heating ferric chloride in hydrogen :



Anhydrous ferrous chloride is soluble in alcohol and ether. It volatilises at a high temperature and the vapour density corresponds with the equilibrium : $\text{Fe}_2\text{Cl}_4 \rightleftharpoons 2\text{FeCl}_2$. On heating in air, ferric chloride volatilises and ferric oxide remains :

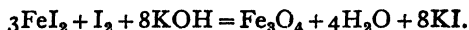


When ferrous chloride is heated in steam hydrogen is evolved :



The hydrated salt is deposited from solutions of iron in hydrochloric acid in bluish-green monoclinic crystals $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ which oxidise slightly and become green in the air.

Ferrous bromide FeBr_2 and ferrous iodide FeI_2 are prepared from the elements and form the crystalline hydrates $\text{FeBr}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeI}_2 \cdot 5\text{H}_2\text{O}$. They are also formed by adding the halogen to iron filings (in excess) in presence of water. If excess of iodine is used, a solution of $3\text{FeI}_2 + \text{I}_2$ is formed, which gives with potassium hydroxide or carbonate a black precipitate of hydrated ferrosferric oxide (p. 188) :



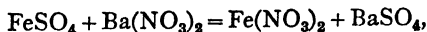
Ferrous oxide FeO is formed as a black powder by reducing ferric oxide with hydrogen at 300° to 500° , or by adding ferrous oxalate (obtained by precipitating ferrous sulphate with ammonium oxalate) to boiling

potassium hydroxide solution. A pyrophoric mixture of ferrous oxide and finely divided iron is obtained by heating ferrous oxalate in absence of air: $\text{FeC}_2\text{O}_4 = \text{FeO} + \text{CO} + \text{CO}_2$. Ferrous oxide is reduced to metallic iron by hydrogen at 700° to 800° .

Ferrous hydroxide $\text{Fe}(\text{OH})_2$ is thrown down as a white precipitate when sodium hydroxide is added to a pure solution of a ferrous salt with absolute exclusion of air. It is insoluble in excess of alkali unless the latter is very concentrated, but dissolves slightly in ammonium salts. It crystallises from concentrated sodium hydroxide solution in flat green prisms and is a definite compound. The precipitate rapidly becomes green in the air from formation of Fe_3O_4 and finally brown, forming $\text{Fe}(\text{OH})_3$.

Ferrous carbonate FeCO_3 occurs as *siderite* or *spathic iron ore* in rhombohedra isomorphous with calcite. It is formed on addition of an alkali carbonate to ferrous salts as a white precipitate, rapidly becoming green and finally brown on exposure to air owing to oxidation to ferric hydroxide. The addition of sugar retards the oxidation. Ferrous carbonate dissolves in water containing carbonic acid forming **ferrous bicarbonate** $\text{Fe}(\text{HCO}_3)_2$, and on exposure to air, ferric hydroxide is precipitated (p. 55). Plants absorb iron from the soil as the bicarbonate.

Ferrous nitrate is formed when iron is dissolved in dilute nitric acid (p. 605) but is best obtained by decomposing ferrous sulphate with barium nitrate in solution :



filtering from barium sulphate and evaporating in a vacuum desiccator over sulphuric acid, when crystals with $6\text{H}_2\text{O}$ separate. They readily oxidise to ferric nitrate.

Ferrous phosphate $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is sparingly soluble and occurs as the mineral *vivianite*. The white precipitate formed from a solution of a ferrous salt and sodium phosphate soon becomes blue or green on exposure to air.

Ferrous sulphide FeS is formed with evolution of heat as a black mass by heating 3 parts of iron filings with 2 parts of sulphur (p. 13). It may be prepared by dipping a white-hot bar of wrought iron into molten sulphur in a crucible. (Cast iron is not attacked.) A mixture of iron filings and sulphur when moistened becomes heated and forms FeS . The mineral *pyrrhotite* or *magnetic pyrites* is often formulated as Fe_7S_8 but apparently it has a composition varying from Fe_7S_8 to Fe_9S_9 .

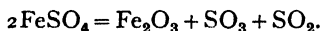
Ferrous sulphide in the pure state is a yellowish crystalline mass with a metallic lustre ; the commercial substance is black or dark grey and contains free iron. It dissolves readily in dilute acids and is used in the preparation of hydrogen sulphide. A greenish-black precipitate of ferrous

sulphide is formed when ammonium sulphide is added to a solution of a ferrous salt, or hydrogen sulphide is passed into ferrous sulphate solution containing sodium acetate. The precipitate dissolves slightly in excess of yellow ammonium sulphide forming a dark greenish-black solution.

Ferrous sulphate FeSO_4 is the most important ferrous salt and is obtained by dissolving iron or ferrous sulphide in dilute sulphuric acid, or by the slow oxidation of marcasite or "coal-brasses" FeS_2 by air in presence of water (*pyrites* is stable in air unless it is first roasted). The common form is *green vitriol* $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, crystallising in monoclinic crystals isomorphous with one form of Epsom salt $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. If a crystal of *white vitriol* $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is placed in the saturated solution *rhombic* crystals of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ isomorphous with that salt are deposited, whilst *blue vitriol* $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ induces the deposition of *triclinic* isomorphous crystals of $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$.

Crystalline hydrates of ferrous sulphate with 6, 3, and $2\text{H}_2\text{O}$ are also known.

By precipitating the solution with alcohol or by heating green vitriol in a vacuum at 140° the monohydrate $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ is formed, and this on heating at 300° in absence of air leaves the white amorphous anhydrous salt. On heating this gives a basic salt and at a red heat it decomposes:



Ferrous sulphate readily forms double-salts with the sulphates of the alkali-metals, $\text{M}_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$. If equimolecular amounts of ferrous sulphate and ammonium sulphate are dissolved to saturation in separate amounts of warm water and the filtered solutions mixed, **ferrous ammonium sulphate** or *Mohr's salt* $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ is deposited on cooling in light bluish-green monoclinic crystals, which may also be deposited in the form of a practically white powder on adding alcohol to the solution (*cf.* $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The crystals are stable in air and the solution (to which a few drops of dilute sulphuric acid are added) is much less easily oxidised by atmospheric oxygen than ferrous sulphate or chloride. *Mohr's salt* is therefore used in volumetric analysis for standardising solutions of potassium permanganate or dichromate; it contains almost exactly one-seventh of its weight of ferrous iron.

Iron dissolves in sulphurous acid without evolution of gas: the solution deposits colourless crystals of **ferrous sulphite** leaving a solution of **ferrous thiosulphate**: $2\text{Fe} + 3\text{H}_2\text{SO}_3 = \text{FeSO}_3 + \text{FeS}_2\text{O}_3 + 3\text{H}_2\text{O}$.

Ferrosoferrous oxide Fe_3O_4 occurs as *magnetite*. It is strongly magnetic and is formed by heating iron to redness in air ("smithy scales") or in steam, or by heating ferric oxide in the electric furnace. The pure oxide

is obtained as a black powder by reducing Fe_2O_3 at 400° in a current of hydrogen and steam. It melts at a very high temperature and is cast into electrodes, which resist acids and chlorine: Hydrated ferrosferric oxide $\text{Fe}_3\text{O}_4 \cdot \text{Aq.}$ or $\text{Fe}(\text{OH})_2 \cdot \text{Fe}_2\text{O}_3$, formed as a black precipitate by adding sodium hydroxide to a mixture of a ferrous and a ferric salt, is magnetic. It dissolves in hydrochloric acid to a green solution, containing FeCl_2 and FeCl_3 . The oxide Fe_3O_4 may be formulated as ferrous ferrite, $\text{Fe}(\text{FeO})_2$.

Iron disulphide FeS_2 occurs as *iron pyrites* and *marcasite*. Pyrites is stable in air, marcasite oxidises in moist air to ferrous sulphate. Pyrites crystallises in the regular system, often in plain or striated cubes; sixty-nine forms have been described. It has a brassy-yellow colour ("fools' gold"), is very hard, striking sparks from steel, and is not magnetic. Marcasite occurs in rhombic crystals, usually in the form of radiating nodules and is white like tin. Pyrites often occurs in coal and is the source of much of the sulphur dioxide formed on its combustion. It is found in masses having the form of wood, roots, etc., and has probably been formed by the reduction of solutions of ferrous sulphate by organic matter. Pyrites on heating in absence of air loses some sulphur:

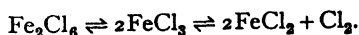


and if heated in air, all the sulphur is burnt to dioxide (p. 552).

Pyrites is insoluble in dilute acids but dissolves readily in concentrated nitric acid (with separation of sulphur) or in *aqua regia*. Artificial FeS_2 is formed by heating ferrous sulphide with sulphur, by passing hydrogen sulphide over iron oxides or chlorides heated to redness, or by heating a mixture of ferric oxide, ammonium chloride and sulphur. FeS_2 contains *ferrous* iron. The iron atoms and $-\text{S}-\text{S}-$ groups are arranged in a rock salt lattice (p. 94), the centres of the S_2 groups and the iron atoms occupying the places of the sodium and chlorine ions. The marcasite lattice is slightly different.

FERRIC SALTS

Ferric chloride FeCl_3 is the most important ferric salt. It sublimes in anhydrous iron-black crystals with a green iridescence on heating iron or ferric oxide in chlorine. The apparatus of Fig. 160 may be used. The vapour density at 444° corresponds with Fe_2Cl_6 . At higher temperatures dissociation occurs:



In solutions in alcohol and ether the molecular weight corresponds with FeCl_3 . The anhydrous chloride is also soluble in benzene. These solutions show the bright yellow colour of FeCl_3 . Aqueous solutions containing excess of hydrochloric acid are also bright yellow.

Aqueous solutions of ferric chloride are produced by dissolving ferric hydroxide in hydrochloric acid, or by saturating a solution of ferrous chloride with chlorine. On evaporation and cooling yellow hydrated

crystals are deposited which are readily soluble in water. Ferric chloride solution is used as a styptic, *i.e.* in stopping bleeding: it coagulates the blood, forming a clot. The solution is strongly acid, due to hydrolysis (p. 239). On heating the hydrated salts hydrochloric acid is evolved and a basic salt or finally ferric oxide is left.

Garnet-red double salts are formed from ferric chloride and other chlorides, *e.g.*



Fig. 242 is from Roozeboom's experiments. *AB* is the freezing point curve from pure ice at *A* to the eutectic of $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ and ice at *B* (-55°). *BC* is the solubility curve of the 12-hydrate, *C* being the melting-point of this pure hydrate. This is a maximum on the curve, which is characteristic of a definite compound. Beyond *C* the solution takes up more salt, *CD* showing the lowering of freezing point by adding ferric chloride. At *D* a new hydrate $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ appears, its melting point 32.5° being at *E*. The curve *FGH* belongs to the hydrate $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ melting at *G*, and the curve *HJK* to the hydrate $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ melting at *J* (73.5°). The curve beginning at *K* (66°) is the solubility curve of an-

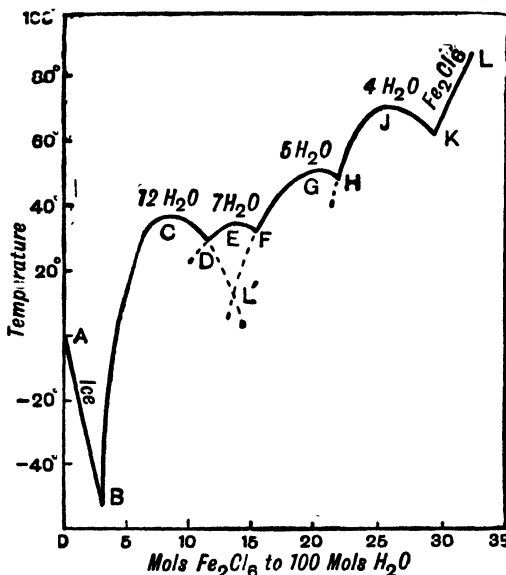


FIG. 242.—Hydrates of ferric chloride.

hydrous ferric chloride, which runs up very steeply to a point well off the diagram.

Ferric fluoride FeF_3 is a white difficultly soluble salt, only slightly ionised in solution. It forms double fluorides, *e.g.* Na_3FeF_6 analogous to cryolite. The bromide FeBr_3 is formed similarly to the chloride, but the iodide does not appear to exist.

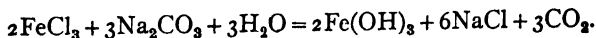
Ferric oxide exists in two crystalline forms: $\alpha\text{-Fe}_2\text{O}_3$ (*haematite*) and $\gamma\text{-Fe}_2\text{O}_3$, which passes into $\alpha\text{-Fe}_2\text{O}_3$ at a red heat. The only definite crystalline hydrate of ferric oxide is $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which also exists in two forms, *goethite* or $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and *lepidocrocite* or $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The mineral *limonite*, formerly regarded as $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is goethite with adsorbed water. The other supposed hydrated oxides are amorphous and have the character of gels.

A brown ferric hydroxide gel is precipitated from a solution of a ferric salt by adding ammonium chloride and ammonia; it is slimy in the cold but becomes flocculent on boiling. It is soluble in dilute acids but practically insoluble in water and alkalis, and is the form in which iron is separated in quantitative analysis. On prolonged boiling in contact with the solution the precipitate becomes sparingly soluble in acids. The gel on drying forms a dark brown mass of indefinite composition. On ignition this loses water, sometimes with the production of a glow, and Fe_2O_3 is formed, which in this state is nearly insoluble in acids. Red varieties of ferric oxide are formed by igniting ferrous sulphate in the air, and are used as paints or as a polishing powder (*rouge, crocus, colcothar*).

Colloidal ferric hydroxide is obtained by dissolving freshly precipitated ferric hydroxide in a concentrated solution of ferric chloride and dialysing. The blood-red solution (*dialysed iron*) is readily precipitated by salts. On adding concentrated hydrochloric acid, the solution is *slowly* converted into yellow ferric chloride. If glycerin, sugar, tartaric acid, etc., are added to a solution of a ferric salt the latter is not precipitated by ammonia, but a clear brown colloidal solution is formed.

Ferric oxide is a feebly acidic oxide and forms salts with strong bases. If strongly heated with sodium carbonate sodium ferrite NaFeO_2 ($\text{Na}_2\text{O}, \text{Fe}_2\text{O}_3$) is formed (see p. 280).

Ferric carbonate does not appear to exist, ferric hydroxide being precipitated by an alkali carbonate from a ferric salt solution:



Ferric nitrate is obtained by dissolving iron in fairly concentrated nitric acid or in *warm* dilute nitric acid (p. 605); the dark brown solution (used as a mordant) deposits colourless cubic crystals of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or monoclinic crystals of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

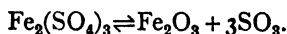
Ferric phosphate $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is obtained as a white precipitate insoluble in acetic acid but soluble in mineral acids, when sodium phosphate is added to a ferric salt in solution. It is used in the separation of phosphates in qualitative analysis. A basic salt is the mineral *dufrenite* $\text{Fe}_2(\text{OH})_2\text{PO}_4$.

Ferric sulphide Fe_2S_3 is formed as a yellow mass with a metallic lustre by gently heating iron with sulphur, by heating ferric oxide in H_2S below 100° , or by the action of H_2S on moist ferric hydroxide in absence of alkali. It is thrown down as a black precipitate by the action of excess of ammonia and ammonium sulphide on a solution of a ferric salt; with excess of ferric salt a mixture of 2FeS and S is formed.

Ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$ is formed by boiling ferrous sulphate with dilute sulphuric and nitric acids, when nearly pure nitric oxide is evolved (p. 485), but is most easily obtained by evaporating ferrous sulphate with concentrated sulphuric acid :



Anhydrous ferric sulphate is a yellowish-white powder dissolving only very slowly in water but ultimately forming a very concentrated solution. This is brown-red owing to hydrolysis but becomes paler on addition of sulphuric acid. On heating, ferric sulphate evolves sulphur trioxide :

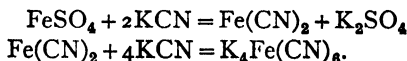


With potassium and ammonium sulphates ferric sulphate forms iron alums, e.g. $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, with a violet colour when pure but often pale yellow owing to the presence of ferric oxide. These are readily soluble in water and are not appreciably hydrolysed. The potassium alum $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ does not crystallise so readily as the ammonium salt.

Ferrates.—A mixture of one part of iron filings and two parts of nitre deflagrates on heating, and the cold product dissolves in water to form a purple solution (Stahl, 1703). This contains potassium ferrate K_2FeO_4 containing 6-valent iron (Fremy, 1841). On boiling a yellow solution of potassium ferrite $\text{K}_2\text{Fe}_2\text{O}_4$ is produced, which rapidly deposits ferric hydroxide. On addition of barium chloride to potassium ferrate solution, fairly stable barium ferrate $\text{BaFeO}_4 \cdot \text{H}_2\text{O}$ is formed as a red precipitate.

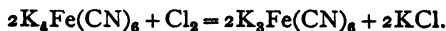
Potassium ferrocyanide.—When nitrogenous organic matter such as horn or leather clippings is fused with potassium carbonate and iron filings and the mass digested with water, the solution deposits on evaporation yellow crystals of potassium ferrocyanide or *yellow prussiate of potash*, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. The addition of a ferric salt to the solution gives a deep-blue precipitate of *Prussian blue*, the first ferrocyanogen compound to be discovered (Diesbach, 1704).

Potassium ferrocyanide is obtained as a by-product in the coal-gas industry (p. 408). It is also formed by adding excess of potassium cyanide to ferrous sulphate solution till the brown precipitate dissolves :

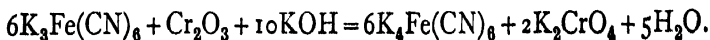


The yellow hydrated crystals are stable in air but on heating form the white anhydrous salt. Silver nitrate gives a white precipitate of silver ferrocyanide $\text{Ag}_4\text{Fe}(\text{CN})_6$.

Potassium ferricyanide.—If chlorine is passed into a solution of potassium ferrocyanide, the ferrocyanide is oxidised to ferricyanide :



The ferricyanide and chloride are separated by crystallisation. Potassium ferricyanide $K_3Fe(CN)_6$ forms anhydrous dark-red monoclinic prisms (*red prussiate of potash*, L. Gmelin, 1822). It is an oxidising agent, converting litharge into lead dioxide, and chromium hydroxide into potassium chromate, on boiling in alkaline solution :

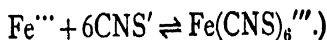


The alkaline solution is reduced by hydrogen peroxide (p. 145).

Prussian blue.—When excess of ferric chloride solution is added to a solution of potassium ferrocyanide, a deep-blue precipitate of **ferric ferrocyanide** $Fe_4^{III}(FeCy_6^{II})_3$ ($Cy = CN$) called *Prussian blue* is thrown down.

The precipitate from potassium ferricyanide and excess of a ferrous salt, called *Turnbull's blue*, is not ferrous ferricyanide (as was once supposed) but is identical with Prussian blue and an interchange of charges must have resulted : $Fe^{II} + FeCy_6^{III} \rightleftharpoons Fe^{III} + FeCy_6^{II}$. No precipitate is formed on mixing solutions of a ferric salt and potassium ferricyanide, a dark-brown colour only being produced.

A solution of a thiocyanate gives with a ferric salt a deep-red solution containing **ferric thiocyanate** $Fe(CNS)_3$; this is decolorised by mercuric chloride, mercuric thiocyanate being formed. (The red colour has also been attributed to a complex ion :



Sodium nitroprusside $Na_2Fe(NO)Cy_5 \cdot 2H_2O$ is a red salt formed by warming potassium ferrocyanide with 50 per cent. nitric acid. It is used as a test for sulphides (p. 550).

The **atomic weight of iron** has been determined by the reduction of ferric oxide (from carefully purified ferric nitrate) in hydrogen ; this is one of the very rare cases in which the analysis of an oxide has been used in an accurate atomic weight determination. Another method used was the determination of the ratio $FeBr_2 : 2AgBr$. The valency is found from the atomic heat and the vapour densities of ferric chloride (p. 609) and iron carbonyl $Fe(CO)_5$.

CHAPTER XXXIV

COBALT AND NICKEL

COBALT

Historical.—The use of cobalt as a constituent of some blue glazes and blue glass made in imitation of lapis lazuli (p. 379) has been established for ancient Egyptian (1375 B.C.) and Babylonian (about 1450 B.C.) specimens by analysis. Most of the ancient blue glazes, however, owe their colour to a compound of copper, $\text{CuO}, \text{CaO}, 4\text{SiO}_2$. Some specimens of Roman blue glass (*e.g.* a piece found at Uriconium) owe their colour to cobalt.

The name *cobalt* is used by Agricola and other German writers for certain minerals which resembled ores of metals, yet did not yield metal with the usual treatment but gave off an arsenical smell. The roasted *cobalt*, called *zaffre* (impure cobalt arsenate), gives on fusion with sand and potassium carbonate a beautiful blue glass called *smalt*. The blue colour, at first believed to be due to arsenic, was shown by Brandt (1735) to come from a new metal and Bergman (1780) investigated its properties.

Occurrence.—The arsenide of cobalt, nickel and iron $(\text{Co}, \text{Ni}, \text{Fe})\text{As}_3$ (in the pure state CoAs_3) is known as *speiss cobalt* or *smaltite*. A similar ore is *linnaeite* $(\text{Co}, \text{Ni}, \text{Fe})_3\text{S}_4$. Cobalt is also found as *cobalt glance* or *cobaltite* $(\text{Co}, \text{Fe})\text{AsS}$, and as *cobalt bloom* $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, but is now mainly obtained from the arsenides and sulphides in the silver ores of Cobalt City, Ontario, from the Belgian Congo, from Queensland, and from New Caledonia where manganese ore containing about 2 per cent. of cobalt oxide occurs. Cobalt is nearly always associated with nickel.

Metallic cobalt is obtained as a grey powder by strongly heating the oxide in hydrogen, or on the large scale by heating the oxide with carbon and limestone in the electric furnace when a fused metal is obtained. The cobalt is separated from a solution of cobalt sulphate (formed from the roasted ore) by adding sodium hypochlorite, which precipitates cobalt peroxide. The metal may also be prepared by the electrolysis of a solution of the sulphate CoSO_4 , containing ammonium sulphate and ammonia.

Cobalt is tenacious and silver-white in colour with a slight bluish cast which nickel has not, is readily polished and shows a high lustre. It is magnetic. Cobalt does not oxidise in air and has been used for plating as it is harder and brighter than nickel. When heated it slowly oxidises

in air. All the oxides are reduced to metal when heated in hydrogen. Cobalt in a finely divided state absorbs hydrogen. The metal dissolves slowly in dilute sulphuric and hydrochloric acids and readily in dilute nitric acid. It can become passive like iron.

Cobalt steel is used for permanent magnets as these can be made much smaller than carbon-steel magnets, and do not become demagnetised. A nickel-aluminium steel, however, has more than twice the magnetic coercivity of cobalt steel. *Stellite* is an alloy of chromium, tungsten and cobalt, very hard and non-corroding, used for surgical instruments. *Festel metal* is an alloy of cobalt, iron and chromium used for cutlery.

COBALT COMPOUNDS

The ordinary salts contain bivalent (cobaltous) cobalt. Tervalent (cobaltic) cobalt salts are usually rather unstable (although the complex compounds, *e.g.* the cobaltammines, are very stable) and include the oxide Co_2O_3 , sulphide Co_2S_3 , fluoride CoF_3 , and the blue sulphate $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ obtained by electrolytic oxidation, which forms unstable alums and is a powerful oxidising agent.

Cobalt chloride CoCl_2 sublimes in blue crystals when the metal is heated in chlorine. The hexahydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is obtained in dark-red deliquescent crystals from a solution of cobalt or the oxide in hydrochloric acid. It forms a number of lower hydrates. The anhydrous salt and the lowest hydrate $\text{CoCl}_2 \cdot \text{H}_2\text{O}$, obtained by gentle heating, are blue in colour. A solution of cobalt chloride is used as a *sympathetic ink*; the writing is almost invisible but becomes blue on holding the paper before the fire. On standing in moist air the colour again disappears. A piece of paper impregnated with cobalt chloride is blue in dry weather and pink in damp weather.

The pink solution of cobalt chloride (which probably contains the hydrated ion $\text{Co}(\text{H}_2\text{O})_6^{++}$) becomes blue on heating or addition of concentrated hydrochloric or sulphuric acid. A complex blue anion CoCl_4^{--} appears to be formed: $2\text{CoCl}_2 \rightleftharpoons \text{Co}^{++} + \text{CoCl}_4^{--}$. Cobalt nitrate solution becomes blue when concentrated hydrochloric acid is added, but not with sulphuric acid.

Cobalt bromide CoBr_2 and iodide CoI_2 are formed from the elements as dark-green and black solids; they form dark-red hydrates with $6\text{H}_2\text{O}$ and lower hydrates which are purple and green, respectively.

Cobaltous oxide CoO is a light-brown powder obtained by heating the hydroxide out of contact with air or Co_3O_4 at 200° in hydrogen. It is a basic oxide forming salts with acids. Cobaltous hydroxide $\text{Co}(\text{OH})_2$ is precipitated by alkali from solutions of cobalt salts: a bluish-violet precipi-

tate is first formed which on standing in presence of excess of alkali and more rapidly on boiling is converted into a pink form.

Cobaltous hydroxide dissolves only in traces in excess of alkali hydroxide but is soluble in excess of ammonia, a yellowish-brown solution being formed which deposits cobaltous hydroxide on dilution, but readily absorbs oxygen from the air to form stable complex *cobaltammines* (p. 618).

On heating cobalt nitrate the product is cobalto-cobaltic oxide Co_3O_4 , which is also formed when cobaltous oxide is strongly heated in air. Black hydrated cobaltic oxide Co_2O_3 is precipitated by hypochlorite from a solution of a cobaltous salt (see p. 108), and with excess of hypochlorite some cobalt dioxide CoO_2 is formed.

Cobalt carbonate CoCO_3 is formed as a pink hydrated precipitate on adding sodium bicarbonate to a cobalt salt solution and allowing to stand. It forms with potassium carbonate a pink double salt $\text{K}_2\text{CO}_3 \cdot \text{CoCO}_3 \cdot 4\text{H}_2\text{O}$, and a bright reddish-purple one of similar formula with sodium carbonate.

The carbonyls $[\text{Co}(\text{CO})_3]_4$ and $[\text{Co}(\text{CO})_4]_2$ are formed only under pressure. The orthosilicate Co_2SiO_4 is present in blue cobalt glass and glazes.

Cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is obtained in pink crystals from a solution of cobalt in dilute nitric acid; it loses water and forms the pink anhydrous salt in a desiccator.

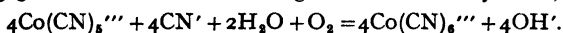
A solution of cobalt nitrate is used in blowpipe analysis. The ignited residue on charcoal is moistened with one drop of dilute cobalt nitrate and reheated. Zinc gives a *green* mass (*Rinman's green*, cobalt zincate CoZnO_3) and aluminium a *blue* mass (*Thenard's blue*, Al_2CoO_4), although blue masses are also produced with phosphates. Magnesia gives a pink mass. Cobalt salts give a beautiful blue borax bead.

Cobaltous sulphide CoS is formed on heating the elements and is precipitated by ammonium sulphide or by hydrogen sulphide in presence of sodium acetate. It is black and although not precipitated by hydrogen sulphide from acid solutions it is insoluble in dilute acids but is soluble in *aqua regia*. Precipitated cobalt and nickel sulphides are apparently $\text{Co}(\text{SH})_2$ and $\text{Ni}(\text{SH})_2$ which absorb oxygen from air. The sulphides Co_2S_3 and CoS_2 are known.

Cobaltous sulphate $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ is isomorphous with $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The crystals have different amounts of water according to the temperature; the solution at 40° to 50° deposits $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ isomorphous with $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$, and when poured into concentrated sulphuric acid it gives $\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$. The anhydrous salt is rose-red. It forms double sulphates with alkali metal and ammonium sulphates, *e.g.*

K_2SO_4 , $CoSO_4 \cdot 6H_2O$, which are isomorphous with corresponding ferrous and nickel salts.

When potassium cyanide is added to a solution of a cobalt salt a reddish-brown precipitate of **cobaltous cyanide** $Co(CN)_2 \cdot 3H_2O$ is thrown down, soluble in excess of cyanide forming a yellow solution of **potassium cobaltocyanide** $K_3Co(CN)_6$, which is thrown down as a deep amethyst-coloured powder by alcohol. If a little acetic or hydrochloric acid is added to the solution and the latter boiled in an evaporating dish for a few minutes, oxidation occurs and **potassium cobalticyanide** $K_3Co(CN)_6$, containing 3-valent cobalt and analogous to the ferricyanide, is formed:



The cobalticyanide forms stable yellow crystals isomorphous with $K_3Fe(CN)_6$. Cobalticyanides give none of the reactions of cyanides or of cobalt, and are not decomposed by concentrated nitric acid.

Potassium nitrite gives with a solution of a cobaltous salt acidified with acetic acid a yellow precipitate of **potassium cobaltinitrite** $K_3Co(NO_2)_6$ (*Fischer's salt*) only slightly soluble in water:



The cobaltinitrite is produced only in acidified solutions; if acetic acid is not added a yellow precipitate of $K_2Co(NO_2)_4$ is formed. Potassium cobaltinitrite is decomposed by ammonium sulphide.

α -nitroso- β -naphthol dissolved in acetic acid gives with cobalt salts a red precipitate; the reagent does not precipitate nickel salts.

On addition of excess of ammonia to a cobalt salt and exposure to air, absorption of oxygen occurs and a brown solution is formed which becomes pink on boiling. The solutions contain complex **cobalt-ammines** which contain 3-valent cobalt, e.g. $[Co(NH_3)_6]Cl_3$. The reaction occurs more rapidly if lead dioxide is added.

Univalent cobalt Co^I is present in the brownish-green solution formed by reducing potassium cobaltocyanide solution with potassium amalgam or electrolytically. It evolves hydrogen at room temperature.

NICKEL

History.—A coin of the Bactrian king Euthydemus (235 B.C.) contains 77.58 per cent. of copper and 20.04 per cent. of nickel, and alloys of copper, zinc and nickel called *paktong* were used in China. A German mineral resembling copper ore from which no copper could be obtained was called *kupfer-nickel* (i.e. "false copper") by Hiärne (1694). In 1751 Cronstedt obtained impure metallic nickel from this ore; the properties of nickel were investigated more thoroughly by Bergman.

Occurrence.—The chief ores of nickel are the cobalt ore *smaltite* $(Ni, Co, Fe)As_2$; *white nickel ore* $NiAs_2$; *kupfer-nickel* or *niccolite* $NiAs$; *nickel glance* $NiAsS$, *millerite* NiS , and the important ores *garnierite*

(Ni,Mg)SiO₃ found in New Caledonia, and *pentlandite* (Fe,Ni)S containing about 2·5 per cent. of nickel found at Sudbury, Ontario. *Nickel ochre* Ni₃(AsO₄)₂·8H₂O also occurs. Nickel is found in meteoric iron, and is also obtained as a by-product in electrolytic copper refining.

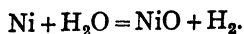
Metallurgy of nickel.—The Sudbury ores (the most important) contain pentlandite, chalcopyrite CuFeS₂ and pyrrhotite (p. 607), which are partly separated by flotation. The pentlandite with some chalcopyrite is roasted, smelted and bessemerised, yielding a *matte* containing copper, nickel and sulphur, with a little iron. This may be worked up to give *monel metal*, containing nickel and copper with some iron and manganese and resembling nickel in colour and properties.

If the *matte* is melted with coke and saltcake (which form sodium sulphide) and poled, two strata separate. The upper layer contains sodium sulphide and cuprous sulphide, the lower layer nickel sulphide NiS. The lower layer is purified and is roasted to nickel oxide NiO, which is reduced by heating strongly with carbon.

Nickel is extracted from Canadian *matte* by the **Mond carbonyl process**, worked in South Wales. The roasted *matte* (still containing some sulphur) is leached with dilute sulphuric acid to remove copper, which is converted into blue vitriol. The residue is reduced at about 330° to 350° by water gas. Nickel oxide but not ferric oxide is reduced at this temperature. The mass is next passed at 50° down a tower provided with shelves and carbon monoxide is passed through, when volatile **nickel carbonyl** Ni(CO)₄ is produced. The gas containing this is passed through a decomposer heated at 180° to 200°. Decomposition occurs and metallic nickel is deposited on nickel pellets kept stirred, the carbon monoxide passing back to the volatiliser: $\text{Ni(CO)}_4 \rightleftharpoons \text{Ni} + 4\text{CO}$.

Nickel is refined by electrolytic deposition from a solution of nickel ammonium sulphate (NH₄)₂SO₄, NiSO₄·6H₂O, a cast nickel block being used as anode and a thin polished sheet of pure nickel as cathode. The anode mud contains platinum metals (which are extracted). The same process is used in nickel-plating, a thin layer of copper being first deposited on iron or steel goods.

Metallic nickel is silver-white with a grey tinge, is hard and malleable and takes a high polish. It is magnetic. Nickel is fairly resistant to pure air but in town air containing acid and soot it rapidly tarnishes and acquires a green patina of basic sulphate, so that nickel-plating is now covered with chromium. The metal is resistant to fused alkalis and is used for crucibles; containers for milk have also been used. Nickel oxidises only very slowly when heated in air and decomposes steam only very slowly at a red heat:



Finely divided nickel absorbs hydrogen and acts as a catalyst in hydrogenation reactions, *e.g.* the absorption of hydrogen by liquid oils containing glycerol esters of unsaturated fatty acids. When treated with hydrogen at 150° to 250° in presence of finely divided nickel these take up hydrogen

and become solid fats. A definite black solid **hydride** NiH_2 , also CoH_2 , FeH_2 and FeH_3 , have been described.

Nickel is used chiefly in the manufacture of *nickel steel*, usually containing about 3.5 per cent. of nickel, of nickel crucibles and tubes, and alloyed with 75 per cent. of copper for coinage. An alloy of copper and nickel is used for coating rifle bullets. *Nichrome*, an alloy of nickel, iron and chromium, melts at a high temperature and is used for electric resistance heaters. *German silver* is an alloy of copper, nickel and zinc.

NICKEL COMPOUNDS

Nickel dissolves in dilute nitric acid, a green solution being obtained. The colour is that of the nickel ion Ni^{++} or $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ and is shown by all the simple salts of nickel. Nickel becomes passive in concentrated nitric acid.

Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is produced by dissolving the metal in *aqueous regia* and evaporating. On heating, the green crystals form yellow anhydrous NiCl_2 .

Alkali hydroxide gives with solutions of nickel salts an apple-green precipitate of **nickel hydroxide** $\text{Ni}(\text{OH})_2$, insoluble in excess but somewhat soluble in ammonia and soluble in ammonium salts forming blue solutions, from which $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ and $\text{Ni}(\text{NH}_3)_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ may be obtained in blue crystals. On heating the hydroxide **nickel monoxide** NiO is obtained as a green mass. This is also formed on strongly heating the nitrate; at a lower temperature a black **sesquioxide** Ni_2O_3 is formed, which liberates chlorine when dissolved in hydrochloric acid. The black precipitate formed by the action of chlorine or hypochlorite on a suspension of nickel hydroxide contains the hydrated **dioxide** NiO_2 and hydrated Ni_2O_3 . Nickel hydroxide is not oxidised by atmospheric oxygen or hydrogen peroxide.

Nickel carbonate $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ is obtained in green crystals by adding nickel sulphate to a solution of sodium bicarbonate saturated with carbon dioxide. A green basic salt is precipitated by sodium carbonate.

A black **nickel nitride** Ni_3N is known. The **nitrate** is formed in grass-green crystals $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on evaporating a solution of the metal or oxide in dilute nitric acid; it is very soluble in water. The anhydrous nitrate cannot be obtained by heating the hydrate, which decomposes (see above) but is formed by the action of nitrogen pentoxide on the hydrate: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 6\text{N}_2\text{O}_5 = \text{Ni}(\text{NO}_3)_2 + 12\text{HNO}_3$.

Nickel sulphide NiS is formed as a black precipitate when ammonium sulphide is added to a solution of a nickel salt. It dissolves slightly in

corresponding places in the other two transitional groups. The atomic weights of cobalt and nickel have been found by the reduction of the oxides, chlorides and bromides in hydrogen and from the ratios $\text{CoCl}_2 : 2\text{AgCl}$ and $\text{NiBr}_2 : 2\text{AgBr}$. The valencies follow from the atomic heats and the vapour density of Ni(CO)_4 , as well as the isomorphism of salts with those of other elements.

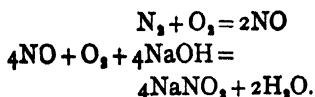
CHAPTER XXXV

THE INERT GASES

Argon.—In 1785 Cavendish noticed that a small residue was left on sparking air with oxygen over caustic potash (p. 475). Until 1894 it was taken for granted that atmospheric nitrogen was a pure substance, but in that year Lord Rayleigh in his accurate determinations of the densities of gases noticed that nitrogen prepared from the atmosphere is slightly denser than that prepared by chemical reactions, *e.g.* from ammonium nitrite. He suspected that an unknown gas was present in the nitrogen. In conjunction with Sir William Ramsay, he prepared a new gas from atmospheric nitrogen by two methods:

1. In Ramsay's method the oxygen of air is absorbed by passing over red-hot copper and the residual nitrogen is repeatedly passed over strongly heated magnesium. The nitrogen is slowly absorbed as magnesium nitride Mg_3N_2 and the unabsorbed residue is argon.

2. In Rayleigh's method a mixture of oxygen and air was passed (Fig. 243) into a 50-litre glass globe provided with heavy platinum electrodes. A discharge was passed between the electrodes and a fountain of sodium hydroxide solution was pumped over the inside of the globe:



The excess of oxygen was absorbed by alkaline pyrogallol.

The gas obtained by these methods was called *argon* (Greek *argon*, inactive), since it was found not to react chemically with any substance.

Argon, krypton and xenon, however, form crystalline hydrates with $6H_2O$ on cooling and compression, the most stable being that of xenon.

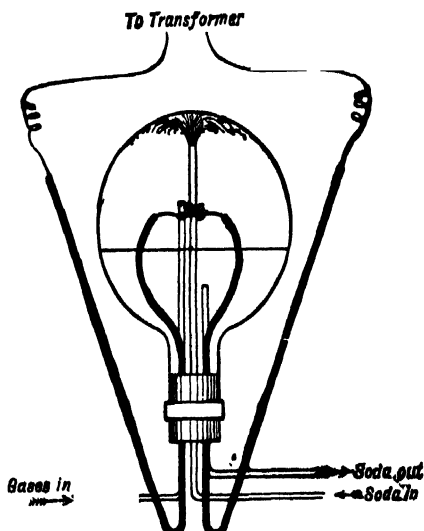


FIG. 243.—Rayleigh's method for the preparation of argon.

The table below gives the percentage composition of *dry* air by *volume* at sea-level; about 1 per cent. of argon is present:

Nitrogen	-	-	-	78.08	Neon	-	-	-	0.0018
Oxygen	-	-	-	20.95	Helium	-	-	-	0.0005
Argon	-	-	-	0.93	Krypton	-	-	-	0.0001
Carbon dioxide	-	-	-	0.03	Xenon	-	-	-	0.00001

Argon is obtained technically from the impure liquid oxygen obtained in plants making nitrogen (p. 120).

This is fed half way up a tall fractionating column with a nest of tubes at the top cooled with liquid nitrogen, when the gas passing on is nitrogen with 50 per cent. of argon. This enters a second similar column, when nitrogen passes out at the top and argon with oxygen impurity collects at the base. The argon is freed from oxygen by passing over red-hot copper.

Commercial argon (*e.g.* 88 per cent. and the rest nitrogen) is used in "gas-filled" electric lamps.

Helium.—In 1868 a spectroscopic examination of the sun during a total eclipse showed a yellow line which did not exactly coincide with the D lines of sodium. Sir Norman Lockyer concluded that it corresponded with an element which he called helium (Greek *helios*, the sun). In 1894 Ramsay, at the suggestion of Miers, examined the gas evolved from *cleveite* (a variety of pitchblende) by heating with dilute sulphuric acid or in a vacuum. It was found by Crookes to give the helium line in the spectrum.

Helium occurs only in minute traces (0.0005 per cent. by vol.) in the atmosphere but larger amounts (up to about 1 per cent.) are present in gases from some mineral springs and particularly from oil wells in America, from which helium is now prepared. The gas is very strongly cooled, when all other gases except helium condense. Helium is also produced in some radioactive changes (p. 266).

Helium is more difficult to liquefy even than hydrogen (it boils at -269°) but has been liquefied and also solidified (by cooling the liquid to -272° under pressure). By special methods, temperatures below 0.001° abs. have been attained by cooling certain salts in the presence of a strong magnetic field in liquid helium and then suddenly removing the magnetic field.

Neon.—In the residue from the evaporation of liquid air Ramsay and Travers in 1898 discovered two other inactive gases, **krypton** (Greek *krypton*, concealed) and **xenon** (Greek *xenos*, the stranger). In crude liquid argon they found helium and a new inactive gas **neon** (Greek *neon*,

new). Neon (at. wt. 20) was specially searched for in order to fill a gap in the periodic system between helium (at. wt. 4) and argon (at. wt. 40).*

Neon is separated by suitable fractionation of liquid air. When an electric discharge is passed through the gas at reduced pressure, it emits an intense orange light, hence neon is used in discharge tubes for advertising and other purposes.

Atomic weights of the inert gases.—Since the inert gases do not form compounds their atomic weights are found by physical methods. The ratio of specific heats $c_p/c_v = \gamma$, which can be calculated from the velocity of sound (u) in a gas from the equation $u^2 = \gamma p / \rho$ (p = pressure, ρ = density), is found to be 1.666 for the inert gases, which shows that their molecules are monatomic (p. 89). The molecular weights found from the gas densities are therefore equal to the atomic weights.

* See Travers, *The Discovery of the Rare Gases*, 1928.

occupies 22.4 litres at 0°C . and 1 atm. pressure, what will be the gas equation in this particular case? Use this equation to calculate the volume of the given mass of oxygen at 91°C . and at a pressure of 0.8 atm.

(Bombay B.A.)

2. The following quantities of gas are contained over mercury in separate measuring vessels: 70.0 c.c. of hydrogen at 15°C . and 720 mm.; 10.0 c.c. of oxygen at 10°C . and 700 mm.; 14.0 c.c. of nitrogen at 20°C . and 760 mm. All are mixed in another vessel at 18°C . and the volume is found to be 94.0 c.c. What is the total pressure in the vessel and the partial pressure of each constituent?

(Bombay B.A.)

3. What is meant by the term Partition (Distribution) Coefficient? Illustrate your answer by reference to the process of extraction with ether. An aqueous solution contains 10 gm. of solute per litre; when 1 litre of the solution is treated with 100 c.c. of ether, 6 gm. of the solute are extracted. How much more of the solute would be extracted from the aqueous residue by a further 100 c.c. of ether? (Assume that the molecular state of the solute is the same in ether and water.)

(C.)

4. How is the solubility of a gas in a liquid expressed? How is it affected by changes of (a) pressure, (b) temperature? How would you determine the solubility of ammonia in water at room temperature and atmospheric pressure?

(C.)

CHAPTER VIII

1. Write a short account of the methods for determining the chemical equivalent of an element, and discuss in detail *one* such method. One gm. of the chloride of a metal dissolved in water was mixed with an excess of silver nitrate solution. The weight of the dried precipitate of silver chloride was 2.110 gm. What was the equivalent of the metal? ($\text{Ag} = 107.88$; $\text{Cl} = 35.46$.)

(L.I.)

2. Discuss the relationship between the laws of chemical combination and the atomic theory. Two oxides of a certain element contain respectively 43.6 and 56.3 per cent. of oxygen. Assign possible formulae to the two oxides.

(C.)

3. "The theory of chemistry, with all its modern developments, is indisputably the theory of Dalton." Discuss and criticise this statement.

(C.)

4. State the law of constant proportions and the law of multiple proportions. Describe the experiments which have been made in order to prove the truth of *one* of these laws.

(C.)

CHAPTER IX

1. The vapour density of the chloride of a metal is 81.5 ($\text{H} = 1$). The chloride contains 34.46 per cent. of metal. The specific heat of the metal is 0.115. Find the *exact* atomic weight of the metal and the formula of the chloride.

(L.S.)

2. By what methods of reasoning have chemists come to the conclusion that the molecular weight of a substance is twice its vapour density?

(B.)

3. Outline the experiments and arguments which have led to the adoption of the formula H_2O for water vapour. Describe *one* of the experiments in detail. (Assume nothing but Avogadro's Rule.) Explain briefly why the combining volumes of hydrogen and oxygen are not in the exact ratio of 2 : 1.

(O.)

When the vapour density of ammonium chloride is determined under ordinary conditions, the results correspond to a molecular formula $N_4H_4Cl_4$. Discuss this, showing how it is to be explained, and describe an experiment in support of your explanation. (C.)

4. What is Mitscherlich's law of Isomorphism? An element forms two oxides, containing 52.0 and 68.4 per cent. of the element respectively. The higher oxide is an acidic oxide and forms a potassium salt isomorphous with potassium sulphate. What is the atomic weight of the element, and what are the formulae of the two oxides? (C.W.)

5. What do you understand by a "crystal"? Indicate briefly some of the directions in which the study of crystals has been of use to chemistry. (O.)

6. Describe in detail how an accurate determination of the equivalent weight of carbon might be carried out. Explain how the atomic weight of carbon may be derived when its equivalent weight is known. (O. & C.)

7. (a) 1.00 gm. of the anhydrous sulphate of a metal, when heated, gave a residue of oxide weighing 0.298 gm. The vapour density of the corresponding chloride was found to be 130 at low temperatures, but fell to half this value at higher temperatures. The specific heat of the metal is 0.21.

(b) 100 c.c. of an elementary gas weigh 0.09 gm. at S.T.P. Its specific heat at constant volume is 0.15, and at constant pressure 0.25.

Calculate the atomic weights of the two elements, making use of all the data, and briefly explain the principles involved. (Proofs of a thermodynamical nature are not required.) (O.)

8. Describe briefly how the relative density (vapour density) of an elementary gas, such as chlorine, may be determined experimentally. Explain fully two lines of argument by which the atomic weight of the element could be deduced when the relative density is known, stating what further data are necessary. Would the value of the atomic weight so deduced be accurate or approximate? (C.)

9. State and explain (a) Avogadro's Law, (b) Graham's law of diffusion of gases. A non-metallic gaseous oxide is found to contain 36.36 per cent. of oxygen. The gas diffuses at the same rate as carbon dioxide. Calculate (a) the equivalent weight of the non-metal, (b) the exact molecular weight of the gaseous oxide. (L.I.)

10. Describe any method used for determining the vapour density of a substance which dissociates on heating.

At 230° the vapour density of phosphorus pentachloride is 4.134 (air = 1). Find the degree of dissociation. What would be the effect of: (i) reducing the pressure, (ii) reducing the temperature, (iii) adding nitrogen to the mixture? (Weight of 1 litre of air at S.T.P. = 1.293 grams.) (L.S.)

CHAPTER X

1. Write a short essay on *one* of the following subjects:

(a) The choice of a suitable indicator in acidimetry.

(b) Valency. (An historical treatment is suggested, and there should be some reference to recent developments.) (O.)

CHAPTER XI

1. Give an account of (a) a method of obtaining pure oxygen in the laboratory, and (b) a modern industrial method of preparing oxygen from

the atmosphere, explaining briefly the principles involved in (b). For what purposes is oxygen used? (L.I.)

2. Describe the preparation of ozonised oxygen. How could you distinguish a mixture of air and ozone from a mixture of air and chlorine? (C.)

3. Write an account of the preparation, properties and probable constitution of ozone. Give three characteristic tests for this substance. (C.W.)

4. How would you prepare a sample of ozonised oxygen? Draw a neat sketch of the apparatus you would use and mention the properties of the gas. When 150 c.c. of a sample of ozonised oxygen were treated with turpentine the volume was reduced by 36 c.c. What changes, if any, would you notice when another 150 c.c. of the same mixture is heated until no further change is noticeable and finally cooled to the original temperature and pressure? (Mysore First Cert.)

CHAPTER XII

1. On what factors does the position of equilibrium between iron and steam and their reaction products depend? How can these factors be controlled in order to give a maximum yield of hydrogen? (L.)

2. Describe the changes which take place when (a) air, (b) steam is passed over heated coke, and explain the bearing of the changes on the method used for the manufacture of water gas. How may hydrogen be prepared on the large scale from water-gas? What are the industrial uses of hydrogen? (O. & C.)

CHAPTER XIII

1. Give an account of the conditions under which water will react with (a) sodium, (b) magnesium, (c) iron, and explain the nature of the products in each case. (L.)

2. How is barium peroxide prepared? How would you prepare from it a pure specimen of hydrogen peroxide? How does hydrogen peroxide react with (a) manganese dioxide, (b) lead sulphide, (c) silver oxide, (d) acidified potassium permanganate? (C.)

3. Describe how you would prepare a fairly concentrated solution of hydrogen peroxide, and give a brief account of its more important reactions. How would you find the concentration of hydrogen peroxide in the solution? (C.)

4. Describe briefly the preparation and properties of ozone and hydrogen peroxide. How have the molecular weights of these substances been determined and what structural formulae have been assigned to them? (L.I.)

5. Five c.c. of a solution of hydrogen peroxide liberated 0.508 gm. of iodine from a solution of potassium iodide. Describe in detail a volumetric method of obtaining such a result. Express the strength of the hydrogen peroxide in terms of (a) gms. of hydrogen peroxide per litre, (b) normality, (c) "volume" strength. (L.I.)

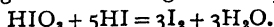
6. Give an account of the changes, if any, which take place when water is allowed to react with *seven* of the following substances: hydrogen chloride, calcium oxide, calcium hydride, phosphorus pentoxide, phosphorus trichloride, carbon tetrachloride, silicon tetrachloride, calcium sulphate hemi-hydrate. (C.)

CHAPTERS XIV-XV

1. How is chlorine prepared in the laboratory? Write an account of the chief chemical and physical properties of chlorine. (L.)
2. Describe the manufacture of chlorine by the Deacon process, and give an account of the theory of the reaction. How is potassium chlorate manufactured from chlorine? (L.I.)
3. What substances are produced when chlorine is passed to saturation into (a) an aqueous solution of ferrous chloride, (b) a cold saturated solution of potassium iodide, (c) a suspension of calcium carbonate in water, (d) ice-cold water. (L.I.)
4. Describe and explain the behaviour of an aqueous solution of chlorine (a) when exposed to sunlight, (b) when distilled, (c) when added to a cold solution of sodium hydroxide, (d) when added to a suspension of chalk, (e) when added to a suspension of yellow mercuric oxide. (L.I.)
5. Describe briefly *two* methods used for the industrial preparation of chlorine. What is the action of chlorine on aqueous solutions of (a) potassium hydroxide, (b) ammonia, (c) ferrous sulphate acidified with sulphuric acid, (d) hydrogen sulphide? (L.)
6. Chlorine was originally known as dephlogisticated muriatic acid and later as oxymuriatic acid. Explain the views which led to the use of these names and why the former was changed to the latter. Describe experiments, if possible the classical ones, to show that the views now held concerning the relationships of chlorine and hydrochloric acid give a better account of the facts. (O. & C.)
7. Give a brief account of the preparation and properties of the salts of the oxyacids of chlorine. How would you determine the molecular formula of any *one* of them? (O. & C.)
8. What is bleaching powder and how is it made? For what purposes is bleaching powder used? How may (a) a solution of hypochlorous acid, (b) chlorine, (c) oxygen, be prepared from bleaching powder? (L.I.)
9. How are chlorine monoxide and chlorine dioxide respectively prepared? What is the effect of heat on each and how does each react with caustic potash? (C.W.)

CHAPTER XVI

1. Give an account of *one* method for the commercial preparation of iodine from natural sources. How, and under what conditions, does iodine react with (a) hydrogen, (b) hydrogen sulphide, (c) mercury, (d) caustic potash solution, (e) sodium arsenite, (f) sodium thiosulphate. (B.)
2. Write an account of the method used for the manufacture of pure bromine. Starting from this element how may solutions of hydrobromic and bromic acids be prepared? Indicate briefly why you think bromine is correctly placed in the Periodic Table. (L.)
3. Describe the method used in the manufacture of bromine. How is potassium bromide obtained from it on the large scale? Describe the preparation in the laboratory of (a) potassium bromate, (b) gaseous hydrogen bromide, from bromine. (L.I.)
4. What experiments would you perform to show that iodic and hydriodic acids react together according to the equation



How would you make use of this reaction to determine the strength of a given solution of sulphuric acid? (L.)

5. Why was fluorine regarded as an element and classed with the halogens before it had been isolated? How was fluorine isolated? Give a brief account of its physical and chemical properties. (L.I.)

6. How may iodine be converted into (a) potassium iodide, (b) an aqueous solution of hydrogen iodide, (c) iodic acid? (C.)

7. Name *two* minerals containing fluorine and state their composition. Describe the preparation of anhydrous hydrogen fluoride. Compare the properties of the hydracids of the four halogens. How are fluorides detected in analysis? (O. & C.)

8. How is fluorine prepared? Give reasons for the procedure adopted. Give a concise account of the chemistry of the element and its more important compounds, noting briefly the features that accord with the group-properties, and paying special attention to the marked deviations therefrom. (C.W.)

CHAPTER XVII

1. State Faraday's Laws of Electrolysis. Describe two experiments in electrolysis, and state in terms of the ionic theory exactly what you infer from the result of each. (1st M.B. London)

2. Give a concise account of the theory of electrolytic dissociation. How does this theory account for the varying strengths of acids? Describe any experiments you have seen which support this explanation. (Q.M.C.)

3. The same electric current is passed through acidulated water and through a solution of the chloride of a metal *X*. The volume of hydrogen liberated was 14.8 litres at S.T.P. and the weight of metal deposited 42 grams. The specific heat of the metal is 0.094. Find the formula of the chloride. (L.S.)

4. Explain and illustrate by examples the meanings of the following terms: electrolytic dissociation, eutectic mixture, exothermic compound, complex ion, basic salt. (C.W.)

5. Describe briefly the theory of electrolytic dissociation. Explain on the basis of this theory the following experiments: (a) The precipitation of sodium chloride from its concentrated solution by passing hydrogen chloride into the solution. (b) The separation of copper from cadmium in Group II by means of potassium cyanide. (c) The alkaline reaction of sodium hypochlorite. (L.S.)

6. State Faraday's laws of electrolysis and define the terms *specific conductivity* and *equivalent conductivity*. How would you determine the equivalent conductivity of a decinormal solution of potassium chloride? (C.)

7. Explain the phenomena which occur when an electric current is passed between electrodes immersed in an aqueous solution of sodium chloride. Describe how solutions of (a) sodium hydroxide, (b) sodium hypochlorite, may be prepared by the electrolysis of a solution of sodium chloride. (C.)

8. Give an account of the application of electrolysis in *two* of the following processes: (a) the isolation of aluminium, (b) the storage of electrical energy in the lead accumulator, (c) the preparation of a dilute solution of sodium hypochlorite, (d) the preparation of potassium persulphate. (C.)

CHAPTER XVIII

1. Explain the origin of the term *colloidal solution* and give an account of the chief properties which distinguish colloidal from true solutions.

Describe briefly how you would prepare colloidal solutions of (a) platinum, (b) silicic acid, (c) ferric oxide. (L.)

2. What do you understand by the osmotic pressure of a substance in solution and how is it determined experimentally? According to Pfeffer a 4 per cent. solution of sugar showed an osmotic pressure of 2082 mm. of mercury at 15° C. Calculate the molecular weight of the sugar. (C.W.)

3. Write an account of the experimental determination of molecular weights of dissolved substances by the freezing point method. A solution of 2.02 gm. of an organic acid dissolved in 50 gm. of acetic acid lowered the freezing point by 1.215° C. Find the apparent molecular weight of the acid. (Molecular depression of freezing point for acetic acid, referred to 1000 gm. = 3.9°.) (L.I.)

4. Write a short essay on *one* of the following : (a) thermal dissociation, (b) osmotic pressure, (c) the colloidal state. (L.I.)

5. State how you would prepare pure colloidal solutions of *two* of the following : ferric hydroxide, silicic acid, silver, and give an account of the distinctive features of such solutions. A calcium chloride solution was made up to such a strength that the addition of 1 c.c. to a gold solution just caused coagulation. What would you expect to observe if, instead of calcium chloride, solutions of equimolar strength of (a) NaCl, (b) AlCl₃ were used? How would the prior addition of a little gelatine solution to the gold solution affect these results? (B.)

6. State the laws governing the lowering of the freezing point of a solvent by a dissolved substance, and describe how you would carry out an experiment to determine the molecular weight of a substance, by observation of the depression of the freezing point.

0.2 gm. of acetic acid was dissolved in 20 gm. each of (a) water, (b) benzene, and the depressions of freezing points were respectively 0.310° C. and 0.432° C. Calculate the apparent molecular weight of acetic acid in the two cases and comment on the results. Under what other conditions does acetic acid exhibit an analogous behaviour? Molecular depressions for 100 gm. of solvent are : water 18.5° C. and benzene 51.2° C. (B.)

7. Describe some method of determining the boiling-point of a dilute solution of a non-volatile solute for comparison with that of the pure solvent. What laws have been found to hold with regard to the boiling-points of dilute solutions? Calculate the concentration of an aqueous solution of urea, CO(NH₂)₂, which would boil at 100.17° C. under standard pressure. What would be the osmotic pressure of this solution at 0° C.? (Molecular constant for water = 5.2° C. per 100 gm.) (O. & C.)

CHAPTER XIX

1. What is meant by saying that the reaction between hydrogen and iodine is reversible? At 360° C., there are present in equilibrium 1.445, 0.935, and 9.55 gm. mol. per lit. of hydrogen, iodine, and hydrogen iodide, respectively. Calculate the equilibrium constant for the reaction. Use this constant to find the composition of the equilibrium mixture at 360° that would be obtained from initial concentrations of 1 gm. mol. per lit. of hydrogen and iodine. (O. & C.)

2. Explain Ostwald's dilution law for weak electrolytes. How is it used for the determination of the relative strength of an acid? (Bombay Inter.)

3. Describe carefully and explain experiments you have seen illustrating (a) the relative strengths of acids, (b) dialysis, (c) mass-action, (d) the

mechanism of the neutralisation of an acid by a base according to the theory of ions. (L.I.)

4. What is meant by the strength of an acid, and what explanation is offered of the varying strengths of acids in aqueous solution? How may the strengths of acids be compared? Arrange the following acids in order of diminishing strength: hydrobromic, acetic, nitric, sulphuric, phosphoric. (L.)

5. What is meant by the following statements:

- (a) The eutectic point of ice and salt is -23°C .
- (b) The solubility product of silver chloride in water is 1.5×10^{-10} .
- (c) The dissociation constant for acetic acid is 1.8×10^{-5} .
- (d) The equilibrium constant for the reaction between alcohol and acetic acid is 4. (O. & C.)

6. State the law of "solubility product" and state how far it is supported by experimental evidence. Explain why (a) zinc sulphide is precipitated from an alkaline but not from an acid solution; (b) copper is not precipitated by hydrogen sulphide in the presence of potassium cyanide; and (c) magnesium hydroxide is precipitated from magnesium sulphate by ammonia, but not by ammonium chloride and ammonia. (C.W.)

7. Discuss concisely *three* of the following facts:

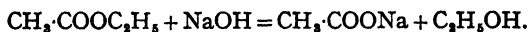
- (a) Iodine is more soluble in potassium iodide solution than in water.
- (b) Ferric oxide can be reduced to the metal by being heated with powdered aluminium, but not with powdered silver.
- (c) The solubility product of barium sulphate is numerically the square of the solubility of this compound (in gm. mol. per litre), granted it is completely dissociated in solution.
- (d) Aluminium hydroxide is soluble both in dilute acid and in sodium hydroxide solution. (O. & C.)

8. Describe fully, and explain, the effects of varying the conditions of temperature and pressure upon the following reactions:

- (a) $2\text{HI} = \text{H}_2 + \text{I}_2$.
- (b) $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$.
- (c) $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$. (O. & C.)

9. What do you understand by the statement that the "strength" of sulphuric acid is only about 60 per cent. of that of hydrochloric acid in $N/2$ solutions? How do you reconcile this statement with the fact that when these acids are neutralised by sodium hydroxide, the "heats of neutralisation" are nearly identical? Explain why (a) calcium oxalate, which is insoluble in water, dissolves in dilute hydrochloric acid, and (b) a solution of potash alum is acid, whilst one of potassium carbonate is alkaline, towards litmus. (B.)

10. State the law of mass action and explain the term *active mass*. Ethyl acetate and sodium hydroxide, present in aqueous solution in equimolecular proportions, were allowed to react at a fixed temperature according to the equation:



After a given time 7.66×10^{-3} gram-molecules per litre of ethyl acetate remained, and the rate of reaction was 3.17×10^{-4} gram-molecules per litre per minute. After a further interval of time the concentration of ethyl acetate had fallen to 5.40×10^{-3} gram-molecules per litre. Calculate the rate of reaction at this instant. (C.)

11. State Le Chatelier's theorem. A gas *A* dissociates into two simpler gases *B* and *C*, the dissociation being an endothermic process. Discuss, with the aid of Le Chatelier's theorem, the influence of (a) temperature, (b) pressure upon the equilibrium. (C.)

CHAPTER XX

1. Give a general account of the method of classification of the elements according to the Periodic Law. On what grounds may the inclusion of the following pairs of elements in the same group in each case be justified : (a) nitrogen and antimony, (b) sulphur and chromium? (L.)

2. What do you understand by the terms "covalent" and "electrovalent" bonds? Give two examples each of compounds containing covalent bonds only, and of compounds containing electrovalent bonds only, giving their electronic formulae. Compare the typical properties of these two classes of compounds with special reference to the examples chosen. (C.W.)

3. Explain the advantages and disadvantages of classifying elements as metals or non-metals from the standpoint of their position in the Periodic Table, their physical properties and the chemical properties of their oxides and chlorides. What problems are raised in an attempt to classify the following elements as metals or non-metals : (a) hydrogen, (b) aluminium, (c) arsenic, (d) chromium? (L.)

4. Give a concise statement of the Periodic Law. Illustrate the change of chemical properties of elements in a group of the Periodic Table with increasing atomic weight by considering (a) chlorine and iodine, (b) carbon and silicon. (L.S.)

5. The second period of the Periodic Table is as follows :

Element	-	Ne	Na	Mg	Al	Si	P	S	Cl
Atomic Number	-	10	11	12	13	14	15	16	17
Atomic Weight	-	20.18	23.00	24.32	26.97	28.06	31.02	32.06	35.46
Isotopes	-	22	23	26	27	30	31	36	37
		20		25		29		34	35
				24		28		32	

Explain this table. Discuss briefly the valency of these elements from the standpoint of the electronic theory. (C.W.)

CHAPTER XXI

1. Describe an electrolytic method for the preparation of metallic sodium. What action have (a) ammonia, (b) oxygen, (c) chlorine, on metallic sodium? Describe the conditions under which each reaction takes place. (L.I.)

2. Adduce evidence to show that an aqueous solution of ammonia contains the compound NH_4OH . Compare and contrast the behaviour of aqueous solutions of ammonia and caustic soda respectively with solutions of (a) copper sulphate, (b) zinc sulphate, (c) bromine. (C.W.)

3. Give an account of the manufacture from common salt of (a) hydrochloric acid, (b) sodium bicarbonate, (c) caustic soda. How would you estimate the amounts of sodium hydroxide and sodium carbonate in a specimen of commercial caustic soda? (L.I.C.)

4. How is sodium thiosulphate usually prepared? State and explain what happens when an aqueous solution of this salt is added to (a) dilute

P.C.

sulphuric acid, (b) a solution of iodine in aqueous potassium iodide. What use is made of this latter reaction in the laboratory? (C.W.)

5. Describe one method in each case by which (a) sodium carbonate, (b) sodium hydroxide, (c) metallic sodium, may be obtained directly or indirectly from sodium chloride. (C.)

6. Describe a method for the production of sodium carbonate from sodium chloride. State what you observe and explain the changes which take place when a concentrated solution of sodium carbonate reacts with (a) sulphur dioxide, (b) carbon dioxide, (c) ferric chloride solution. (1st M.B. London)

7. Give an account of the action of water on the chlorides of the elements. State reasons for thinking that this action gives a satisfactory distinction between metals and non-metallic elements or otherwise. (O.)

8. Give a short account of the discovery of oxygen by Priestley, of chlorine by Scheele, and of potassium by Davy. (L.I.)

9. What are the main features that distinguish metals from non-metals? Discuss the methods of preparation and principal properties of metallic oxides. (B.)

10. Classify the common metals according to their behaviour with (a) air, (b) water, (c) acids. (L.S.)

CHAPTER XXII

1. Copper, silver and sodium are included in the same vertical column of the Periodic System. Justify this classification by a survey of the properties of the three elements and of their principal compounds. Mention any exceptions to the general similarity shown by these elements. (B.)

2. Explain the chemistry of the extraction of copper from its sulphide. Describe and explain the preparation of the following compounds of copper: (a) cupric chloride, (b) cuprous oxide, (c) cuprous chloride. How does (b) react with the dilute mineral acids? (C.W.)

3. Describe concisely the chemical reactions that take place in the preparation of blister copper from copper pyrites. Starting from metallic copper, describe how you would prepare (i) copper sulphate crystals, (ii) dry cuprous chloride, (iii) cuprous oxide. (C.)

4. How is silver estimated (a) in neutral solution, and (b) in acid solution? Explain the chemistry of the processes you describe. Give a brief account of a method of estimation of silver in a silver coin. (L.)

5. Give an account of the extraction of copper from its ores and state the main uses of this metal. What is the effect of the following reagents on a solution of copper sulphate: ammonium hydroxide, hydrogen sulphide, potassium iodide, potassium cyanide, potassium ferrocyanide, zinc dust? (B.)

CHAPTER XXIII

1. Discuss the physical and chemical properties of the metals of the alkaline earths and their compounds, from the point of view of their inclusion in the same group of the periodic system. (L.I.)

2. What are the principal compounds of calcium occurring in nature, and how is the metal calcium prepared? Show how (a) bleaching powder, plaster of Paris and calcium cyanamide, or (b) glass, cement and mortar, are prepared and used in industry. (Bombay B.A.)

3. Enumerate the most striking points of resemblance and difference among the oxides, hydroxides and salts of calcium, barium and strontium. (C.W.)

4. Starting with the mineral dolomite ($\text{CaCO}_3, \text{MgCO}_3$), how would you prepare, in a state of purity, samples of (a) magnesium sulphate, (b) calcium carbonate? Full details are required. (C.W.)
5. How is calcium carbide usually prepared? Explain carefully how this substance may be used for the purpose of rendering atmospheric nitrogen into a usable form. (C.W.)
6. What are the chief minerals containing magnesium? How is the metal itself isolated? Discuss the chemical relationships of magnesium with calcium and zinc. (O. & C.)
7. What general methods are available for the preparation of metallic salts? Explain why an aqueous solution of magnesium chloride does not yield the anhydrous salt on evaporation. How may anhydrous magnesium chloride be obtained from its aqueous solution? (1st M.B. London)

CHAPTER XXIV

1. How is zinc obtained from its ores? From zinc how would you prepare specimens of anhydrous zinc chloride, crystallised zinc sulphate, and zinc pyrophosphate? (L.I.)
2. Give a general account of the mercurous and mercuric salts. How is Nessler's reagent made and used? (L.I.)
3. How does mercury occur in nature and how is it obtained from its ores? How would you prepare chemically pure mercury from a commercial specimen? (L.I.)
4. By what chemical reactions would you distinguish between *mercurous* and *mercuric* compounds? Starting with metallic mercury, how would you prepare (a) mercurous nitrate, (b) mercurous chloride, (c) mercuric chloride? (O. & C.)
5. Describe the extraction of zinc from its two principal ores, and give an account of its chief technical uses. Summarise the chemical and physical properties of zinc and justify its inclusion in Group 2 of the Periodic Table. (B.)
6. Describe the preparation, starting with metallic mercury, of (a) mercurous nitrate, (b) mercuric iodide, (c) mercuric oxide, (d) sodium amalgam. Give an account of the properties of *one* of these substances. (O. & C.)
7. What is meant by describing zinc as a "more electropositive" metal than copper? Describe experiments by which the fact could be illustrated and, in particular, discuss the behaviour of the oxides of these metals towards hydrogen and that of the metals themselves towards steam. (O.)

CHAPTER XXV

1. From what ore is the metal aluminium usually isolated, and how is the process carried out? Mention the chief properties and applications of the metal. What experiments would you perform in order to illustrate the great affinity of aluminium for oxygen? (L.I.)
2. Describe the production of aluminium from bauxite. How would you obtain specimens of anhydrous aluminium chloride, aluminium oxide, and potash alum from metallic aluminium? (L.I.)
3. Describe and explain what happens when a solution of (a) sodium hydroxide, (b) ammonia, (c) sodium carbonate, is added to a solution of (a) aluminium chloride, (b) zinc chloride. (L.I.)

4. Describe the preparation of pure boric acid from borax. How are the following prepared from boric acid : (a) boron, (b) boron chloride?

(L.S.)

5. How would you demonstrate the truth of the following statements : (a) hydrogen sulphide is a reducing agent, (b) borax is hydrolysed in solution, (c) alumina is an amphoteric oxide, (d) caustic soda contains hydrogen.

(L.S.)

CHAPTER XXVI

1. Give a brief account of the allotropy of carbon, stating how you would prove that the various allotropic forms are actually the same element. Describe the preparation and give the properties of carbon monoxide and carbon dioxide and *either* (a) discuss the technical uses of carbon monoxide as a fuel *or* (b) state how the composition of carbon dioxide has been established.

(B.)

2. Write an essay on *one* of the following :

(a) The use of electricity in chemical industry.

(b) The liquefaction of gases.

(c) Combustion and flame.

(B.)

3. Explain with diagrams the structure of a candle flame, and describe experiments you have seen in support of your explanation. What is the difference between an ordinary candle flame and the Bunsen flame?

(Calcutta Inter.)

4. Describe the preparation of carbon disulphide. Compare and contrast its properties with those of carbon dioxide. How would you show that one is an endothermic and the other an exothermic compound? (C.W.)

5. Describe fully how you would determine the composition and molecular formula of marsh gas. Sketch the apparatus you would employ for this purpose.

(Calcutta Inter.)

6. Give an account of the action of steam on red-hot carbon and show how the reaction has been adapted for industrial use. Name the constituents of water-gas, and indicate briefly how you would determine their proportions in a sample of the gas.

(L.)

7. State three methods by which carbon monoxide may be prepared. Give a general account of the properties of this gas and state its action on (a) metallic nickel, (b) oxygen, (c) chlorine, and (d) an ammoniacal solution of cuprous chloride.

(L.S.)

8. Explain, with an example in each case, the meaning of the following : (a) heat of formation, (b) exothermic compound, (c) heat of combustion, (d) heat of reaction. The heat of formation of carbon dioxide is 94,000 cal. and that of nitrous oxide is -17,700 cal. Calculate the heat of combustion of carbon in nitrous oxide.

(L.)

9. Explain how the number of atoms in the molecules of *two* of the following substances may be determined : ozone, argon, hydrogen sulphide, methane.

(O. & C.)

CHAPTER XXVII

1. Compare the properties of the compounds of lead with those of barium, and explain why, in the Periodic Table, lead is not grouped with barium.

(Allahabad Inter.)

2. How is tin prepared from its ores and purified sufficiently for commercial purposes? How would you prepare specimens of (a) stannous chloride, (b) stannic chloride, (c) sodium stannate, from metallic tin? (L.I.)

3. How is lead obtained from its ore galena? How are the following

compounds prepared from lead : litharge, lead dioxide, lead nitrate, lead iodide? (L.I.)

4. What do you know about the occurrence in nature of silica in the free and combined states? How would you prepare a specimen of pure silica from glass, and determine the percentage of silica in a sample of water glass? (L.I.)

5. Say briefly how the following are prepared from ordinary white sand : (a) silicon, (b) soluble silicic acid, (c) silicon chloride. Describe the principal properties of any *one* of them. (C.W.)

6. Describe in detail how you would prepare the following substances from solder : (a) stannous chloride, (b) stannic oxide, (c) lead peroxide.

Compare, in tabular form, the corresponding oxides of carbon, silicon, tin, and lead, and also the chlorides of tin and lead. (O. & C.)

7. What is the chief ore of tin and how is the metal obtained industrially from the ore? In what two forms does tin exist, and how can their inter-conversion be studied? Describe briefly the results of these studies. What is an alloy? What are the two chief alloys of tin, and what advantages have these alloys over their constituent metals? (C.W.)

8. State Mendeléeff's Periodic Law and discuss the family relationship between carbon, silicon, tin and lead from this standpoint. (B.)

9. How would you distinguish experimentally between (a) hydrogen and carbon monoxide, (b) cuprous chloride and cupric chloride, (c) lead monoxide and lead dioxide, (d) solutions of ferrous sulphate and ferric sulphate? Describe how you would prepare *either* lead monoxide or lead dioxide from red lead. (C.)

CHAPTER XXVIII

1. Describe the preparation of a specimen of pure, dry nitrogen. Give an account of the properties of nitrogen. What differences are there between pure and atmospheric nitrogen? What other gases except oxygen and nitrogen are extracted from the atmosphere and for what purposes are they used? (L.I.)

2. What are the principal constituents of the atmosphere? Describe *either* an experiment by which the proportion of carbon dioxide in the air may be measured, *or* an experiment by which the rare gases may be isolated. (C.)

3. Give an account of the methods used commercially to prepare ammonia from atmospheric nitrogen. Outline the evidence on which the formula NH_3 is based. (L.)

4. Explain fully how you would prepare pure dry ammonia and determine its density. What is the effect of (i) heat, (ii) concentrated sulphuric acid, (iii) barium hydroxide, (iv) sodium amalgam, (v) sodium hypobromite, on ammonium chloride? Give equations. (Madras Inter.)

5. How is nitric acid made (a) in the laboratory, (b) synthetically? What is the effect of adding concentrated nitric acid to (a) antimony, (b) copper, (c) polished iron? How does ordinary concentrated nitric acid differ in composition from fuming nitric acid? (L.I.)

6. How would you prepare a specimen of pure nitric oxide gas? Does nitric oxide support combustion? Give experimental evidence of your answer. What is the action of oxygen on nitric oxide in the absence and in the presence of water? (L.I.)

7. What substances may be produced by the reduction of nitric acid? Mention the conditions under which the reactions take place in each case. (L.I.)

8. On what grounds is the molecular formula NO assigned to nitric oxide? A mixture of 20 c.c. nitric oxide and 60 c.c. of oxygen was exposed to water until the gas phase was free from oxides of nitrogen and the solution was free from nitrous acid. The volume of gas remaining was then 45 c.c. To what extent do these data establish the composition of nitric acid? (C.)

9. Describe the preparation in a reasonably pure state of nitric and nitrous oxides. How may the formula of *either* of these gases be determined? How may nitric oxide be converted into nitrous oxide? (No other compound of nitrogen may be assumed to be available except nitric oxide, and if required must be prepared from it.) (L.)

10. Explain clearly the chemistry of *two* methods by which nitric acid can be prepared on the large scale. How, and under what conditions, does nitric acid react with *three* of the following: copper, phosphorus pentoxide, benzene, phosphorus, magnesium? (C.)

11. Give a detailed account of one process for the manufacture of nitrates from atmospheric nitrogen. State (a) the action of heat on potassium nitrate, ammonium nitrate, silver nitrate; and (b) the action of concentrated nitric acid on lead, copper, iron and phosphorus. What is the modern explanation of the tri- and pentavalency of nitrogen in (for example) ammonia and ammonium chloride? (B.)

12. The element nitrogen can be directly oxidised by oxygen, and directly reduced by hydrogen. Describe how you would yourself prove this statement. Compare the reactions in question with reference to the effects of variation of temperature and pressure. (O. & C.)

13. Give an account of the preparation and properties of nitrogen peroxide, N_2O_4 . Contrast its properties with those of nitrogen trioxide, N_2O_3 . (O. & C.)

14. Discuss the "nitrogen cycle" in nature, and indicate briefly the methods used to restore the nitrogen compounds removed from the soil. (O.)

15. Explain *four* of the following phenomena:

- (a) the alkaline reaction of an aqueous solution of borax;
- (b) the effervescence and turbidity on boiling an aqueous solution of magnesium bicarbonate;
- (c) the glass etching property of a mixture of a fluoride and sulphuric acid;
- (d) the decolorisation of potassium permanganate by the addition of sulphurous acid;
- (e) the turbidity on adding water to crystalline stannous chloride;
- (f) the black precipitate produced by adding ammonium hydroxide to an iodine solution. (L.)

CHAPTER XXIX

1. Describe briefly the properties of white and red phosphorus. How may each form be converted into the other? Starting with phosphorus, how would you prepare: (i) metaphosphoric acid, (ii) phosphorus pentachloride, (iii) sodium hypophosphite, (iv) microcosmic salt? (L.S.)

2. How is phosphorus manufactured on the large scale? Describe the preparation from phosphorus of (a) phosphine, (b) the chlorides of phosphorus, (c) phosphorus pentoxide. What is the action of water on these substances? (L.I.C.)

3. Give an exact account of the preparation of (a) phosphorous acid, (b) phosphoric acid. What is the action of heat on these acids? To what types of salts do they give rise? (L.I.)
4. Give a brief account of the element arsenic, its oxides and chloride. How may arsenic hydride be distinguished from the corresponding antimony compound? (L.I.)
5. Compare the methods of preparation and properties of ammonia, phosphine, and arsine. (O. & C.)
6. Describe briefly the manufacture of red phosphorus from calcium phosphate. What reactions occur (a) when phosphorus trichloride is dissolved in water, (b) when phosphorus pentachloride is dissolved in water? What tests would you make to show that the products of these reactions are present in solution? (C.)
7. Compare the chemical properties of arsenic, antimony, and bismuth, with special reference to their positions in the periodic table. (O. & C.)
8. Give the names and approximate chemical composition of two compounds of arsenic which occur in nature, and state how you would prepare a specimen of the element from one of them. By reference to your laboratory experience compare and contrast (a) arsenic and antimony, (b) arsenates and phosphates. (J.M.B.)
9. Starting from arsenious oxide, how would you obtain (a) sodium arsenite, (b) sodium arsenate, (c) Scheele's green? By what reactions are arsenates distinguished from (i) arsenites, (ii) phosphates? (1st M.B. London.)
10. Phosphorus, arsenic, antimony and bismuth are classified together. Justify this grouping by a consideration of the properties of their binary compounds with hydrogen, oxygen, and chlorine. (O.)
11. Discuss the action of water on (a) sodium peroxide, (b) nitrogen peroxide, (c) phosphorus pentachloride, (d) antimony trichloride, (e) aluminium chloride. (L.)

CHAPTER XXX

1. What, and where situated, are the sources of the sulphur used in industrial chemistry? Describe briefly one process used in its extraction. State how you would prepare sulphur trioxide in the laboratory, and explain the principles on which a good yield depends. How would you obtain from sulphur trioxide (a) liquid sulphur dioxide, (b) a crystalline specimen of potash alum? (B.)
2. Give a diagram of the "Lead Chamber" process for the manufacture of sulphuric acid, and describe briefly the chemical reactions involved. Describe in detail how you would estimate the percentage of SO_4 radical in a soluble sulphate. (C.)
3. Give an account of the preparation and properties (including stability) of the more important allotropic modifications of sulphur. What is the action of the following substances on the common allotropic form of sulphur: (a) chlorine, (b) concentrated sulphuric acid, (c) copper, (d) hydrogen? (L.)
4. How is hydrogen sulphide prepared? Explain why this gas may be considered to be (a) a reducing agent, and (b) a dibasic acid. This gas is an undesirable constituent of coal gas. How may its presence in coal gas be detected and how may it be removed? (C.W.)
5. Describe how you would prepare crystals of sodium thiosulphate, starting with sodium and sulphur. Explain the use of this salt in volu-

metric analysis and in photography. When chlorine water is added to a solution of sodium thiosulphate, each molecule of the salt reacts with 8 atoms of chlorine. Write an equation to represent the chemical change, and describe briefly how you would test the truth of the statement. (O.)

6. What is the evidence for regarding the formula of sulphuric acid as H_2SO_4 ? Suggest a structural formula for this compound, giving your reasons for it. (O. & C.)

7. Describe the "Contact Process" for the manufacture of sulphuric acid. What action has sulphuric acid on (a) mercury, (b) carbon, (c) potassium ferrocyanide, (d) oxalic acid? State in each case the conditions under which the reactions described take place. (L.I.)

8. Describe the behaviour of the metals copper and zinc towards (a) dilute hydrochloric acid, (b) nitric acid, (c) cold dilute sulphuric acid, (d) hot concentrated sulphuric acid. (L.I.)

9. Give all the arguments you can which agree with the fact that oxygen and sulphur fall in the same group of the Periodic Table. (L.S.)

10. Describe and explain what happens when roll sulphur is heated in a glass flask to the boiling point. What different varieties of sulphur exist, how are they prepared, and what are their properties? (L.I.)

11. How is sulphuretted hydrogen prepared? How may it be purified? What is the nature of a solution of this gas in water and what is the action of caustic soda on the solution? What takes place when this gas is passed through acidified solutions of the following: silver nitrate, arsenic chloride, ferric chloride, potassium permanganate? (B.)

CHAPTER XXXI

1. What is the chief ore of chromium? Explain how, starting with this ore as raw material, you would obtain (a) potassium chromate, (b) chromium trioxide Cr_2O_3 , (c) chromic anhydride, (d) chromium. For what purposes is chromium mainly employed? (L.I.)

2. In the periodic system sulphur and chromium occur in the same group. Justify this by considering the chemical properties of the two elements. (L.S.)

3. How would you prepare *three* of the following substances: pure nitric oxide, silica (from glass), cuprous chloride (from copper), chrome alum (from potassium dichromate), lead peroxide (from lead). (O.)

4. How is potassium dichromate obtained on an industrial scale from chrome iron ore? Describe the preparation in the laboratory of (a) chromium trioxide (CrO_3), (b) anhydrous chromic chloride, (c) chrome alum, (d) chromyl chloride, (e) potassium chlorochromate. (L.)

5. Write an account of the manufacture, properties and uses of the metal chromium. How may the following be prepared in the laboratory from potassium dichromate: potassium chromate, chrome alum, chromic anhydride, chromyl chloride? State the different valencies exhibited by chromium in its compounds, and give the name and formula of one substance in illustration of each. (B.)

CHAPTER XXXII

1. Describe the preparation of *either* potassium dichromate or potassium permanganate. Give an account of the reactions of these two substances in the presence of dilute sulphuric acid with (a) hydrogen peroxide, (b) ferrous sulphate, (c) potassium iodide. (C.)

2. Describe briefly the industrial methods of preparation and the chief uses of (a) calcium chloride, (b) alum, (c) phosphorus, (d) plaster of Paris, and (e) potassium permanganate. (C.W.)
3. Describe concisely the laboratory preparation of the following reagents: (a) barium chloride from barytes, (b) lead acetate from galena, (c) potassium permanganate from pyrolusite. State, in detail, how you would estimate the purity of any one of the above products. (B.)
4. What is the action of *heat on*: potassium hydrogen fluoride, micro-cosmic salt, potassium permanganate, calcium nitrate, calomel; of *concentrated hydrochloric acid on*: manganese dioxide, potassium dichromate, bleaching powder, potassium chlorate, lead dioxide? (Q.M.C.)

CHAPTER XXXIII

1. Describe *one* method of preparation and the chief properties of *three* of the following compounds: chromyl chloride, sodium thiosulphate, potassium ferrocyanide, cuprous oxide. (C.)
2. Distinguish between double salts, complex salts, and mixed crystals (isomorphous mixtures). Give *two* examples of each type. Describe how you would show that ferrous sulphate forms a double salt with ammonium sulphate, but mixed crystals with magnesium sulphate. (O.)
3. What are the principal ores used in the extraction of iron? State how iron is converted into steel and give in parallel columns a comparative account of the properties of cast iron, wrought iron and steel. Describe how you would prepare from iron wire specimens of ferrous ammonium sulphate and anhydrous ferric chloride. (B.)
4. Describe the production of "pig iron" from iron ore and explain the chemical reactions involved in the process. How are the following substances prepared: (a) potassium ferrocyanide, (b) potassium ferri-cyanide, (c) anhydrous ferric chloride. (L.)
5. "Iron is bivalent in the ferrous salts and trivalent in the ferric salts." Explain clearly what you understand by this statement. Describe how, starting with metallic iron, you would prepare ferrous and ferric sulphates. By what reactions could you distinguish the two salts? (O.)

CHAPTER XXXIV

1. Explain the following processes:
 - (a) The electrolytic purification of copper.
 - (b) The purification of mercury by allowing it to trickle through dilute nitric acid.
 - (c) The use of carbon monoxide in the purification of nickel. (O. & C.)
2. Give an outline of the chemistry of the processes for obtaining any *two* of the following metals from their ores: zinc, copper, iron, nickel. Mention any by-products that are obtained, and indicate briefly their uses. (C.W.)
3. Give an account of the occurrence of nickel and of its extraction from its ores. How would you test a *sample* of nickel for traces of cobalt? (O.)

CHAPTER XXXV

1. Write short essays on *two* of the following subjects: (a) Work on the composition of water 'up to and including Lavoisier's; (b) Black's researches on lime and the alkalis; (c) Scheele's researches on combustion; (d) the discovery of the inert gases. (L.)

2. Describe the methods by which argon was isolated from the atmosphere. Discuss the theoretical and experimental reasons for assigning to this gas a monatomic molecule. (C.)

3. Write an account of the modern methods of liquefying gases, with special reference to the principles involved. (Technical *details* are not required.) Indicate how the rare gases are obtained from liquid air, and mention the uses to which any of them, obtained thus, have been put. (O.)

4. In what way has it been proved that atmospheric nitrogen is not a pure substance? How has the atomic weight of the other main constituent been determined? What other gases are present in atmospheric nitrogen? (L.I.)

ANSWERS

Chapter VII

1. $22.4 \times 1 = 273 \times 0.082$; 37.34 lit.
2. 731 mm.; H_2 542 mm., O_2 77 mm., N_2 112 mm. 3. 2.4 gm.

Chapter VIII

1. 32.47 .
2. M_2O_3 ; M_2O_5 .

Chapter IX

1. 55.92 ; MCl_3 .
4. 52 ; MO_2 , M_2O_3 .
7. At. wts. 26.98 and 20.16 .
9. 14 ; 44 .
10. 0.74 .

Chapter XI

4. 168 c.c.

Chapter XIII

5. 13.6 gm.; $0.8N$; 4.48 vols.

Chapter XVII

3. XCl_3 .

Chapter XVIII

2. 344.9 .
3. 129.7 .
6. 59.7 ; 118.5 (association).
7. 1.96 gm. in 100 gm. water; 7.317 atm.

Chapter XIX

1. 0.196 gm. mol. H_2 and I_2 , 1.608 gm. mol. HI per litre.
10. 1.576×10^{-4} .

Chapter XXVI

8. $129,400$ cal.

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